

# Batteries for Portable Devices

G. Pistoia



# **BATTERIES FOR PORTABLE DEVICES**



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# BATTERIES FOR PORTABLE DEVICES

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## Preface

This overview on battery systems for portable electric and electronic devices is broad but, of course, not exhaustive. However, the reader can find in the 177 references enclosed the possibility to get a deeper insight in the topics he is interested in.

All batteries currently used have been reviewed, from zinc-carbon to lithium-ion, but those having a major impact on portable electronics have been overweighed.

This book is application-oriented. The basics of each battery, *i.e.* electrode materials and processes, electrolytes and cell construction, are described, but emphasis is placed on the performance of the various systems in their applications. A list of commercial batteries is provided for each system along with the devices they usually power.

This book also aims at providing some information on how to get the most from a battery and how to avoid safety risk. The more skilful readers will also have a chance to make their own choice when replacing the batteries of their devices.

This overview also includes topics normally skipped in books of this type: a) small fuel cells and capacitors as complementary (or alternative) power sources; b) collection and recycling of used batteries; c) market trends, with special reference to secondary batteries for consumer electronics.

Rome, October 2004

Gianfranco Pistoia

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# Contents

## Chapter 1. Basic Battery Concepts

1.1. Cells and Batteries: Components	1
1.2. Some Definitions	3
1.3. Practical Cells	7
1.3.1. More Details on Cell Design	13
1.4. Cell Interconnection	15

## Chapter 2. Characteristics of Batteries for Portable Devices

2.1. Common Portable Electric and Electronic Devices and Their Batteries	17
2.2. Summarizing the Criteria of Choice of Primary and Secondary Batteries for Portable Devices	22

## Chapter 3. Battery Standard and Sizes

3.1. Designation of Primary Cells	29
3.2. Designation of Secondary Cells	29
3.3. Performance Tests	31

## Chapter 4. Primary Batteries

4.1. Introduction	33
4.2. Zn-Carbon Batteries	34
4.2.1. Cell Construction and Materials	35
4.3. Alkaline Batteries	39
4.3.1. Electrode Materials and Processes	41
4.3.2. Cell Construction	42
4.3.3. Cell performance	43
4.4. Zinc/Silver Oxide Batteries	47
4.4.1. Cell Materials and Electrode Reactions	49
4.4.2. Cell Construction and Performance	51
4.5. Zinc/Air Batteries	52
4.5.1. Cell Materials and Construction	52
4.5.2. Electrode Reactions	53
4.5.3. Discharge Characteristics, Sizes and Applications	54
4.6. Comparison of the Characteristics of Primary Aqueous	

Batteries	55
4.7. Lithium Batteries	55
4.7.1. Classification of Primary Lithium Batteries	58
4.7.2. Li/MnO <sub>2</sub> Batteries	58
4.7.2.1. Materials and Electrode Reactions	59
4.7.2.2. Cell Construction and Performance	60
4.7.3. Li/CF <sub>x</sub> Batteries	63
4.7.3.1. Materials, Electrode Reactions, Cell Types and Performance	63
4.7.4. Li/FeS <sub>2</sub> Batteries	66
4.7.5. Li/SO <sub>2</sub> Batteries	70
4.7.5.1. Materials and Electrode Reactions	71
4.7.5.2. Cell Construction and Performance	71
4.7.6. Li/SOCl <sub>2</sub> Batteries	72
4.7.6.1. Materials and Electrode Reactions	72
4.7.6.2. Cell Construction and Performance	73
4.8. Comparison of Primary Lithium Batteries	75

## Chapter 5. Rechargeable Batteries

5.1. Introduction	77
5.2. Sealed Lead-Acid Batteries	78
5.2.1. Cell Materials and Electrode Reactions	78
5.2.2. Cell Construction and Performance	80
5.3. Sealed Nickel-Cadmium Batteries	83
5.3.1. Cell Materials and Electrode Reactions	84
5.3.2. Cell Construction and Performance	87
5.4. Nickel-Metal Hydride Batteries	96
5.4.1. Materials and Electrode Reactions	96
5.4.2. Cell Construction and Performance	101
5.4.3. Charging the Ni-MH Battery	104
5.4.4. Cycle and Battery Life	107
5.4.5. Battery Types and Applications	108
5.5. Rechargeable Alkaline Zn/MnO <sub>2</sub> Batteries	109
5.6. Rechargeable Lithium Batteries (with Li-Based Negative Electrodes)	114
5.6.1. Li/Li <sub>x</sub> MnO <sub>2</sub> Batteries	115
5.6.2. Li/V <sub>2</sub> O <sub>5</sub> Batteries	117
5.6.3. Li/Nb <sub>2</sub> O <sub>5</sub> Batteries	117
5.6.4. Li/S Batteries	118
5.7. Lithium-Ion Batteries	119

5.7.1. Carbons	120
5.7.2. Positive Electrodes	125
5.7.3. Liquid Electrolytes	128
5.7.4. Cell Construction and Performance (with Liquid Electrolytes)	129
5.7.5. Li-ion Batteries with Polymeric Electrolytes	137
5.7.6. Applications	142
5.7.7. Care of Li-ion Batteries	143
5.8. Comparison of Secondary Batteries for Portable Devices	146

## **Chapter 6. Batteries for Medical and Special Applications**

6.1. Batteries for Cardiac Rhythm Management Devices	147
6.1.1. The Li/I <sub>2</sub> Battery	149
6.1.2. The Li/Silver Vanadium Oxide (SVO) Battery	150
6.2. Other Medical Applications	153
6.3. Batteries for Special Applications	156
6.3.1. Batteries for Microsensors	156
6.3.2. Batteries for Smart Cards and Tags	160
6.3.3. Examples of Peculiar Battery Uses	161

## **Chapter 7. Battery Safety, Management and Charging**

7.1. Correct Handling	163
7.2. Mechanical and Thermal Safety Devices	164
7.3. The Electronic Battery Control	166
7.3.1. Ordinary ('Non-smart') Battery Charge and Management	167
7.3.1.1. Linear Regulator Chargers (Cradle Chargers)	167
7.3.1.2. Switching Regulator Chargers (Built-in Chargers)	168
7.3.1.3. The Complete Power Management	169
7.3.2. The Smart Battery System and the System Management Bus	170
7.3.2.1. Downsides of the Smart Battery	179
7.3.2.2. Battery Chemistry vs. Management	180
7.4. Is Electronic Control Always Necessary?	183
7.5. Examples of Commercial Chargers	184
7.6. Safety Tests and Certifications	186



## **Chapter 8. Energy Sources Supporting, or Substituting, Batteries**

### **A. Small Fuel Cells**

8.1. Introduction	193
8.2. Basics of PEM Fuel Cells	194
8.3. Single Cell and Cell Stack	198
8.4. Technical Challenges in Fuel Cells for Portable Electronics	203
8.5. Fuel Cell Miniaturization	205
8.6. Fuel Cell Prototypes	206
8.7. Comparison of Batteries and PEM Fuel Cells	209

### **B. Small Supercapacitors**

8.8. Introduction	210
8.9. Types of Supercapacitors	212
8.10. Characteristics of Available Supercapacitors	215
8.11. Advantages and Limitations in the Use of Supercapacitors	218
8.12. Applications of Supercapacitors	219

## **Chapter 9. Spent Battery Collection and Recycling**

9.1. Introduction	225
9.2. Where do Spent Portable Batteries Go?	231
9.3. Collection and Sorting of Spent Batteries	233
9.4. Battery Recycling	236
9.4.1. Aqueous Primary Batteries	236
9.4.2. Nickel-Cadmium and Nickel-Metal Hydride Batteries	237
9.4.3. Lithium and Lithium-Ion Batteries	238
9.4.4. Lead-Acid Batteries	240
9.4.5. Batteries from Electronic Waste	242
9.5. Regulatory Issues for Battery Disposal and Recycling in the U.S.A. and E.U.	243

## **Chapter 10. World Battery Market**

10.1. General Trends	247
10.2. The Market of Rechargeable Batteries for Portable Devices	248
10.3. Lithium-Ion Batteries	252
10.4. Small Fuel Cells	256

**Appendices**

A. Standard Electrode Potentials	259
B. Frequently Used Symbols and Their Relations	261
C. Acronyms Used in Electronics and Mentioned in This Book	262
D. Glossary	263
E. Safety Considerations	270
F. Examples of Battery Chargers, State of Charge Indicators and Battery Protection Circuits	280
G. 1. Battery Companies	283
2. Fuel Cell Companies	285
3. Supercapacitor Companies	285

<b>References</b>	287
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<b>Subject Index</b>	293
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## Chapter 1

# BASIC BATTERY CONCEPTS

### 1.1. Cells and Batteries: Components

A *cell* is the basic electrochemical unit converting the chemical energy stored in it into electrical energy. A *battery* is composed, strictly speaking, of two or more such cells connected in series or parallel. However, the term battery has evolved, especially in the language of the end user, to indicate the product powering a device, regardless of the fact that it contains one or more cells.

A cell converts its chemical energy into electricity by virtue of electrochemical reactions occurring at its electrodes. If such reactions are irreversible, the cell (battery) is termed primary, whereas if they are reversible the cell (battery) may be recharged and is termed secondary.

A cell is based on three active components:

- *Negative electrode*. This is the place where a chemical element (M) or a compound undergoes an electrochemical oxidation during cell discharge (e.g.  $M \rightarrow M^+ + e^-$ ). The electrode is then called *anode*. As indicated in Figure 1.1a, the electron so formed moves through the external cell circuit to reach the opposite electrode. However, if the cell is rechargeable, the above reaction can be reversed (Figure 1.1b), a reduction occurs and the electrode is then called *cathode*.
- *Positive electrode*. The electron from the negative electrode gives rise to an electrochemical reduction (e.g.  $X + e^- \rightarrow X^-$ ) as the cell discharges. Thus, the electrode functions as a *cathode*. In a rechargeable cell, the corresponding oxidation occurs during charge, so that the electrode will be an *anode*.
- *Electrolyte*. During cell operation, the electrolyte allows motion of cations and anions towards electrodes of opposite signs, so closing the circuit. The electrolyte may be an aqueous or a nonaqueous solution of salts, alkalis or acids, but polymeric or solid electrolytes may be used as well.

It is customary to term the negative electrode anode, and the positive electrode cathode for all kinds of batteries, but this is obviously correct for primary batteries only. For rechargeable batteries, as pointed out above, the terminology should be reversed during charge, or, to avoid confusions, the terms *negative electrode* or *positive electrode* should always be used. This will be done throughout this book.

The criteria of electrode selection for practical batteries are rather stringent, thus excluding potentially appealing anode-cathode couples. The material for an electrode should possess most of these requisites (for many of them, more details will be later provided):

- high potential
- limited potential variation during battery discharge
- low weight, thus a high electrochemical equivalent (*e.g.* in ampere-hours/kg [Ah/kg]), and high density, this giving a high volumetric capacity (Ah/L)
- capability of sustaining appreciable currents
- easy synthesis and processibility into a practical electrode
- chemical stability towards the other battery components (especially the electrolyte)
- electrochemical stability in the operating voltage range of the battery
- low cost
- low toxicity

The electrolyte should correspond to these requisites:

- good ionic conductivity and very low, if any, electronic conductivity
- operability in a wide temperature range
- chemical and electrochemical stability
- low flammability and toxicity
- low cost

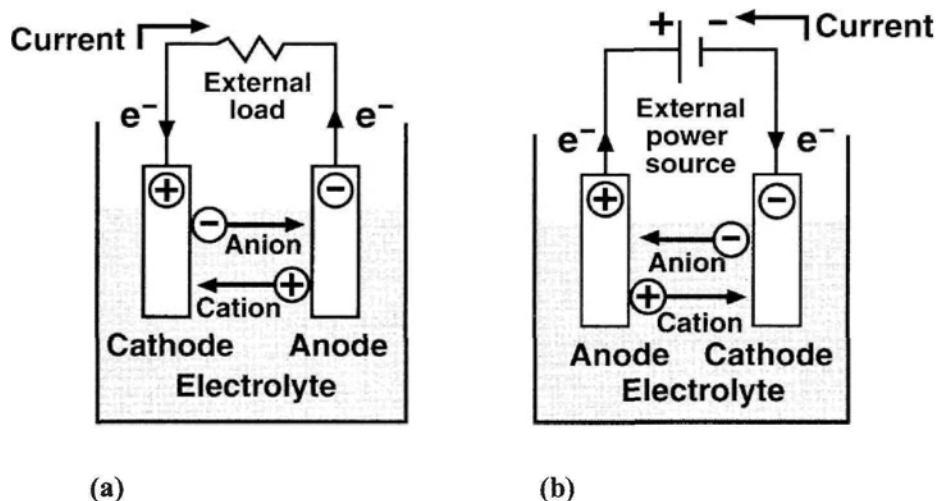


Figure 1.1. Battery operation upon discharge (a) and charge (b). (From Ref.1)

## 1.2. Some Definitions

A cell has a voltage (potential) which is given by the difference of the potentials of the two component electrodes. An individual potential cannot be measured, so that each electrode potential is referred to that of a conventional electrode, usually the hydrogen electrode. The potential of a standard hydrogen electrode, so called because it is measured in standard conditions, is set at zero volts. If the electrode that is being measured with respect to the standard hydrogen electrode is also in standard conditions, its potential will also be referred to as standard:  $E^\circ$  (see Appendix A for more details about standard potentials).

The reversible voltage of a cell, or open circuit voltage (OCV), is just:

$$E_{\text{cell}} = E_{\text{pos}} - E_{\text{neg}} \quad (\text{V})$$

If the electrode potentials of the above equation are standard, the cell potential is also standard ( $E^\circ_{\text{cell}}$ ). This is a good starting point to predict the voltage of a cell with given electrodes. However, the real voltage also depends on such factors as temperature and concentrations of the active materials. Table 1.1 summarizes values of voltage, capacity and energy for the most popular battery systems.

Table 1.1 includes fuel cells, not mentioned so far. Like batteries, fuel cells convert chemical energy into electrical energy through electrochemical reactions occurring at the negative and positive electrode. However, in fuel cells the active materials are fed to the electrodes, in a fluid form, only when the cell is operating. The supporting electrodes are not consumed but have a catalytic activity allowing for the reduction/oxidation reactions to take place. As shown in Table 1.1, the anodic materials are typical fuels, *e.g.* hydrogen or methanol, and the cathodic active material is oxygen. The combined reactions produce water or water and carbon dioxide, *i.e.* an electrochemical combustion occurs in these cells.

Fuel cells are promising power sources for portable devices, and so they will be extensively dealt with in Chapter 8.

Table 1.1 identifies a battery with these basic parameters: voltage (V), specific capacity (Ah/kg), specific energy (Wh/kg) and energy density (Wh/L). Each parameter has a fixed theoretical value, while in operating conditions this value changes to a variable extent. In this book, several other tables, from different sources, list specific energy and energy density for each cell. The data often refer to cells from different manufacturers tested in non-standardized conditions, this explaining some discrepancies. The battery voltage has already been defined. The specific capacity may be calculated from the equivalent

Table 1.1. Voltage, capacity and energy of major battery systems. (Adapted from Ref. 2)

Battery type	Anode	Cathode	Reaction mechanism	Theoretical values <sup>a</sup>				Practical battery <sup>b</sup>		
				Voltage	Electrochemical equivalents		Specific energy	Nominal voltage	Specific energy	Energy density
				V	g/Ah	Ah/kg	Wh/kg	V	Wh/kg	Wh/L
Primary batteries										
Leclanché	Zn	MnO <sub>2</sub>	$\text{Zn} + 2\text{MnO}_2 \rightarrow \text{ZnO} \cdot \text{Mn}_2\text{O}_3$	1.6	4.46	224	358	1.5	85 <sup>(3)</sup>	165 <sup>(3)</sup>
Alkaline MnO <sub>2</sub>	Zn	MnO <sub>2</sub>	$\text{Zn} + 2\text{MnO}_2 \rightarrow \text{ZnO} + \text{Mn}_2\text{O}_3$	1.5	4.46	224	358	1.5	145 <sup>(3)</sup>	400 <sup>(3)</sup>
Zn/Ag <sub>2</sub> O	Zn	Ag <sub>2</sub> O	$\text{Zn} + \text{Ag}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 + 2 \text{Ag}$	1.6	5.55	180	288	1.6	135 <sup>(5)</sup>	525 <sup>(5)</sup>
Zinc/air	Zn	Ambient air	$\text{Zn} + 1/2\text{O}_2 \rightarrow \text{ZnO}$	1.65	1.22	820	1353	1.5	370 <sup>(5)</sup>	1300 <sup>(5)</sup>
Li/SOCl <sub>2</sub>	Li	SOCl <sub>2</sub>	$4\text{Li} + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + \text{S} + \text{SO}_2$	3.65	3.25	403	1471	3.6	590 <sup>(3)</sup>	1100 <sup>(3)</sup>
Li/SO <sub>2</sub>	Li	SO <sub>2</sub>	$2\text{Li} + 2\text{SO}_2 \rightarrow \text{Li}_2\text{S}_2\text{O}_4$	3.1	2.64	379	1175	3.0	260 <sup>(4)</sup>	415 <sup>(4)</sup>
Li/MnO <sub>2</sub>	Li	MnO <sub>2</sub>	$\text{Li} + \text{Mn}^{\text{IV}}\text{O}_2 \rightarrow \text{Mn}^{\text{III}}\text{O}_2(\text{Li}^+)$	3.5	3.50	286	1001	3.0	230 <sup>(4)</sup>	535 <sup>(4)</sup>
Li/(CF) <sub>n</sub>	Li	(CF) <sub>n</sub>	$n\text{Li} + (\text{CF})_n \rightarrow n\text{LiF} + n\text{C}$	3.1	1.42	706	2189	3.0	250 <sup>(4)</sup>	635 <sup>(4)</sup>
Li/I <sub>2</sub> <sup>(1)</sup>	Li	I <sub>2</sub> (P2VP)	$\text{Li} + 1/2\text{I}_2 \rightarrow \text{LiI}$	2.8	4.99	200	560	2.8	245	900
Secondary batteries										
Lead-acid	Pb	PbO <sub>2</sub>	$\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$	2.1	8.32	120	252	2.0	35	70 <sup>(6)</sup>
Edison	Fe	Ni oxide	$\text{Fe} + 2\text{NiOOH} + 2\text{H}_2\text{O} \rightarrow 2\text{Ni(OH)}_2 + \text{Fe(OH)}_2$	1.4	4.46	224	314	1.2	30	55 <sup>(6)</sup>
Nickel-cadmium	Cd	Ni oxide	$\text{Cd} + 2\text{NiOOH} + 2\text{H}_2\text{O} \rightarrow 2\text{Ni(OH)}_2 + \text{Cd(OH)}_2$	1.35	5.52	181	244	1.2	35	100 <sup>(4)</sup>
Nickel-zinc	Zn	Ni oxide	$\text{Zn} + 2\text{NiOOH} + 2\text{H}_2\text{O} \rightarrow 2\text{Ni(OH)}_2 + \text{Zn(OH)}_2$	1.73	4.64	215	372	1.6	60	120
Nickel-hydrogen	H <sub>2</sub>	Ni oxide	$\text{H}_2 + 2\text{NiOOH} \rightarrow 2\text{Ni(OH)}_2$	1.5	3.46	289	434	1.2	55	60
Nickel-metal hydride	MH <sup>(2)</sup>	Ni oxide	$\text{MH} + \text{NiOOH} \rightarrow \text{M} + \text{Ni(OH)}_2$	1.35	5.63	178	240	1.2	75	240 <sup>(4)</sup>
Lithium-ion	Li <sub>x</sub> C <sub>6</sub>	Li <sub>(1-x)</sub> CoO <sub>2</sub>	$\text{Li}_x\text{C}_6 + \text{Li}_{(1-x)}\text{CoO}_2 \rightarrow \text{LiCoO}_2 + \text{C}_6$	4.1	9.98	100	410	4.1	150	400 <sup>(4)</sup>
Lithium- manganese dioxide	Li	MnO <sub>2</sub>	$\text{Li} + \text{Mn}^{\text{IV}}\text{O}_2 \rightarrow \text{Mn}^{\text{IV}}\text{O}_2(\text{Li}^+)$	3.5	3.50	286	1001	3.0	120	265

Table 1.1 (continued)

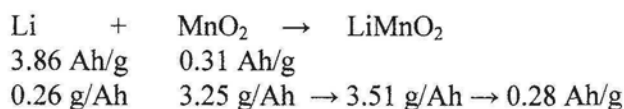
Fuel cells							
H <sub>2</sub> /O <sub>2</sub>	H <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub> + 1/2O <sub>2</sub> → H <sub>2</sub> O	1.23	0.336	2975	3660
H <sub>2</sub> /air	H <sub>2</sub>	Ambient air	H <sub>2</sub> + 1/2O <sub>2</sub> → H <sub>2</sub> O	1.23	0.037	26587	32702
Methanol/O <sub>2</sub>	CH <sub>3</sub> OH	O <sub>2</sub>	CH <sub>3</sub> OH + 1/2O <sub>2</sub> → CO <sub>2</sub> + 2H <sub>2</sub> O	1.24	0.50	2000	2480
Methanol /air	CH <sub>3</sub> OH	Ambient air	CH <sub>3</sub> OH + 1/2O <sub>2</sub> → CO <sub>2</sub> + 2H <sub>2</sub> O	1.24	0.20	5020	6225

- a. Based on active anode and cathode materials only, including O<sub>2</sub> but not air (electrolyte not included).
- b. These values are for single cell batteries based on identified design and at discharge rates optimized for energy density, using midpoint voltage.
1. Solid electrolyte battery (Li/I<sub>2</sub> (P2VP)).
  2. MH = metal hydride, data based on 1.7% hydrogen storage (by weight).
  3. Cylindrical bobbin-type batteries.
  4. Cylindrical spirally-wound batteries.
  5. Button type batteries.
  6. Prismatic batteries.



weight of each electrode materials. The equivalent weight of a material is defined as the ratio between its atomic or molecular weight and the number of electrons involved in the electrochemical reaction. So, for the simple reaction:  $M + e \rightarrow M^+$ , the atomic weight of the metal  $M$  coincides with its equivalent weight. An equivalent weight produces, during reaction, one faraday (F) of electricity, that is 96490 coulombs (Q) or 26.8 ampere-hours (Ah). The latter number is just the ratio  $96490/3600$ , where 3600 is the number of seconds in 1 hour. The Ah produced by 1 gram of material (electrochemical equivalent in Ah/g) is obtained by dividing 26.8 by its atomic or molecular weight.

An example of calculation of the theoretical capacity of a battery, once the electrochemical equivalents of the electrode materials are known, is given here. Let us refer to the primary Li/MnO<sub>2</sub> battery, which is characterized by the reaction:  $\text{Li} + \text{MnO}_2 \rightarrow \text{LiMnO}_2$  (Figure 1.2).



This is a purely theoretical value, as only the weight of the anode, Li, and the cathode, MnO<sub>2</sub>, are taken into account. The weight of such components as electrolyte, separator, battery case, connections, protection circuit, current collectors, and electrode additives (binders and conductors) is not included.

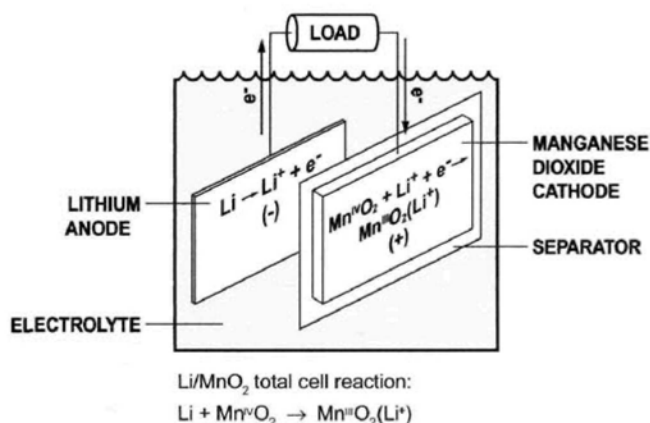


Figure 1.2. Reactions at the positive and negative electrode and total cell reaction for a primary Li/MnO<sub>2</sub> cell. (From Ref. 3)

A battery powering a portable device has to occupy a limited volume. In other words, it is even more important to know the capacity this battery can deliver per unit volume ( $\text{Ah}/\text{cm}^3$ ). This can be obtained from the density of the active materials. For instance, the specific capacity of Li,  $3.86 \text{ Ah/g}$ , reduces to  $2.08 \text{ Ah}/\text{cm}^3$ , once the Li density,  $0.54 \text{ g}/\text{cm}^3$ , is considered.

By multiplying the capacity of a battery (calculated on a weight or on a volume basis) by the theoretical battery voltage, one obtains the theoretical specific energy ( $\text{Wh/kg}$ ) or the energy density ( $\text{Wh/L}$ ).

### 1.3. Practical Cells

As stated above, the theoretical capacity and energy values do not take into account the weight or volume of the other battery components. Furthermore, a cell cannot be discharged at its theoretical voltage due to polarization phenomena at the electrodes and ohmic losses (see below for more details). In terms of capacity, the theoretical one can hardly be exploited, as the cell is never discharged to zero volts and stoichiometric imbalances often occur, *i.e.* one of the electrode materials is in excess, this increasing the overall weight.

With these premises, the actual energy delivered by a battery is only about 20-40% of the theoretical value (Table 1.1). One has to consider that the practical values of the table have been obtained with batteries discharged at moderate currents, so to optimize their energy output, but more severe conditions would remarkably lower these values.

When a current ( $I$ ) is drawn from a battery, the operating voltage is lower than the theoretical one because of: 1) polarization losses at the electrodes, and 2) ohmic losses ( $IR$ ) due to the overall resistance ( $R$ ) of electrodes and electrolytes.

The electrode polarization is made up of two components:

- activation polarization: this is an intrinsic property of the electrode material and measures how difficult is, from a kinetic viewpoint, its charge transfer reaction (*e.g.*,  $\text{M} + e \rightarrow \text{M}^{\cdot}$ )
- concentration polarization: this is related to accumulation or depletion of ions near the electrodes. During a reduction or oxidation reaction, ions are either formed at the electrode (*e.g.*  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e$ ) or are needed for the electrode reaction to take place (*e.g.*  $\text{Li}^+$  ions for the reduction of  $\text{MnO}_2$ ). If ion diffusion away from the electrode, or towards it, is slow, a drop in potential occurs.

Polarizations losses are responsible for a lower voltage on discharge ( $V_d$ ) and a higher voltage on charge ( $V_c$ ) with respect to the open circuit voltage (OCV) of the cell, *i.e.* the voltage measured in the absence of current:

$$V_d = \text{OCV} - \eta_+ - \eta_- - IR$$

$$V_c = \text{OCV} + \eta_+ + \eta_- + IR$$

where  $\eta_+$  and  $\eta_-$  are the polarization at the positive and negative electrode, respectively. Polarization and ohmic losses are more evident when the battery is submitted to high discharge or charge rates. Each battery, based on the nature and amount of its active electrode materials, has a nominal (or rated) capacity,  $C$ , in Ah. The rate at which a battery is charged/discharged is a multiple of the nominal capacity. Normally, but not always, the rated capacity is measured at rates of  $C/5$  or lower. To give an example, a battery delivers its nominal capacity of 1 Ah if a discharge at 0.2 A lasts 5 hours. The general relation between a given discharge (or charge) current and the rated capacity of the battery may be applied:

$$C_d \text{ or } C_c = \text{current/rated capacity}$$

Higher  $C_d$  or  $C_c$  values correspond to lower capacities. In Figure 1.3, the operating voltage of a cell under discharge is shown. It can be remarked that all three factors contributing to the departure of the real voltage from OCV, *i.e.*  $\eta_+$ ,  $\eta_-$  and  $IR$ , tend to increase with current.

The percentage of capacity withdrawn from a battery in a given discharge, related to the total battery capacity, is called depth-of-discharge (DOD). The state-of-charge (SOC) measures how much capacity remains in the battery. The current flowing in the battery is often related, especially at the laboratory level, to the surface or weight of the electrodes. Therefore, it could be given in  $\text{mA}/\text{cm}^2$  or in  $\text{mA}/\text{g}$  (the last one is the weight of an active electrode material).

When a secondary cell is recharged, that is when the reactions occurring at the single electrodes are made to occur in the opposite directions, electrical energy is restored in the form of chemical energy. The charge  $Q_c$  (coulombs or Ah) necessary to do this is always greater than the charge  $Q_d$  delivered on discharge. This is determined by incomplete conversion of the charging current into useful chemical energy, as side reactions, such as corrosion and gas production, may occur. The charge/discharge efficiency may be expressed as coulombic efficiency:

$$\text{Eff}_C = \text{Ah}_{\text{discharge}}/\text{Ah}_{\text{charge}}$$

or as energy efficiency:

$$\text{Eff}_E = V_{\text{discharge}} \cdot \text{Ah}_{\text{discharge}}/V_{\text{charge}} \cdot \text{Ah}_{\text{charge}} = \text{Wh}_{\text{discharge}}/\text{Wh}_{\text{charge}}$$

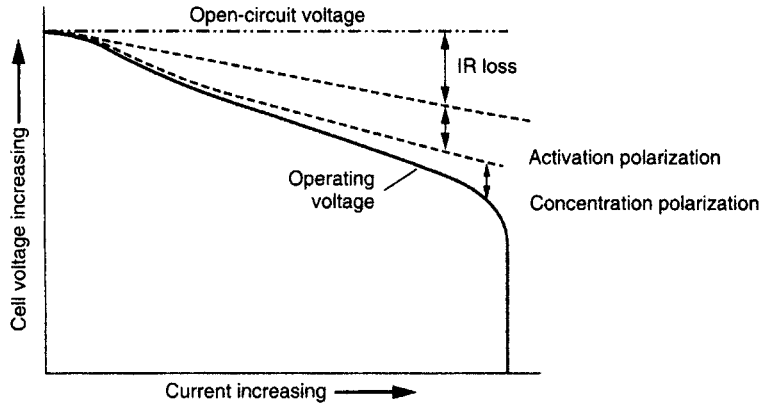


Figure 1.3. Effect of current on the departure of a cell operating voltage from OCV. (From Ref. 4)

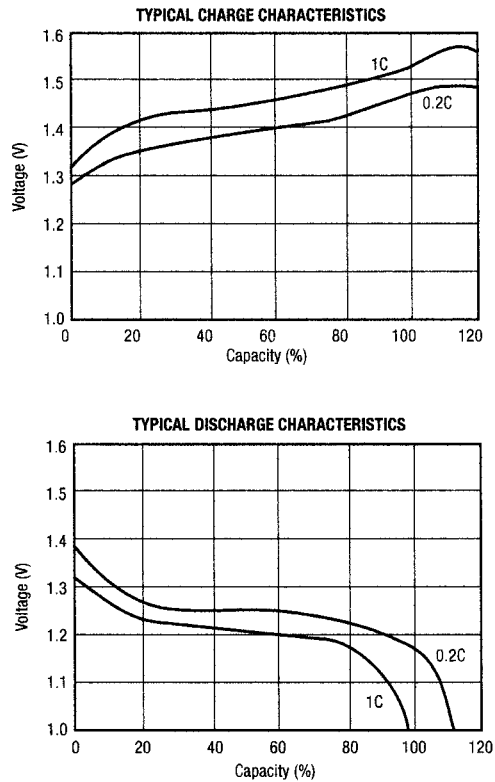


Figure 1.4. Charge and discharge curves, at two different rates, for a nickel-metal hydride (Ni-MH) battery. (Courtesy of Eagle Picher)

In the latter formula, the voltages on charge or discharge are average values. Both the energy and capacity efficiencies depend on such parameters as current density, end voltages, temperature, cell construction and age, *etc.* Figure 1.4 shows typical charge and discharge curves for a Ni-MH battery. At the 0.2C rate,  $\text{Eff}_C$  is 93%, while at the 1C rate it becomes 80%. A rated capacity (100%) practically coinciding with that measured at the 1C rate (98%) is noteworthy.

For a given discharge (or charge) rate, the performance of a battery depends on such factors as:

- *Temperature of operation.* As the temperature decreases, the battery gives a reduced capacity at a lower voltage, as shown in Figure 1.5 for a lithium-ion cell. Indeed, both the ohmic loss  $IR$  and the electrode polarizations increase. On the other hand, too high temperatures may enhance self-discharge phenomena, electrolyte decomposition, and high internal pressure. Each battery has an interval in which it can be used (*e.g.*  $-20$  to  $60^\circ\text{C}$  for primary  $\text{Li/MnO}_2$ ).
- *Type and extent of discharge (charge).* A battery can be discharged continuously or intermittently. Especially if the charge current is high, an intermission can allow the battery to recover its potential through a reduction of the polarization phenomena. Therefore, an intermittent discharge can last longer (see Figure 1.6). In a continuous discharge, pulses at higher rates may be superimposed, *e.g.* during the use of cellular phones or computers. This regime also reduces the cell performance. For secondary batteries, the depth of each discharge is also very important. At high DOD, the battery will prove progressively difficult to recharge, as the electrodes tend to deteriorate.

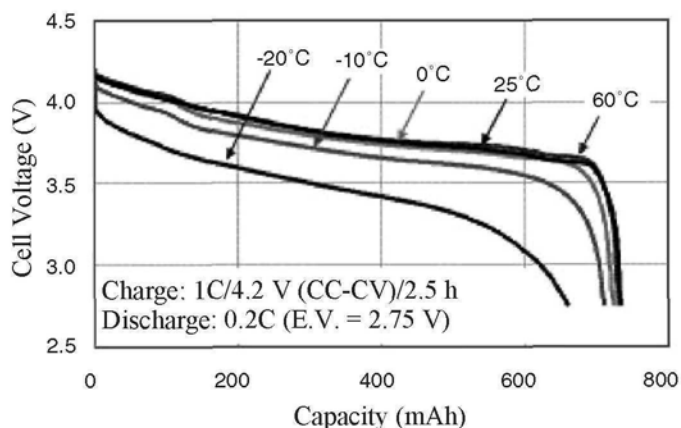


Figure 1.5. Discharge curves of a lithium-ion cell as a function of temperature. (From Ref. 5)

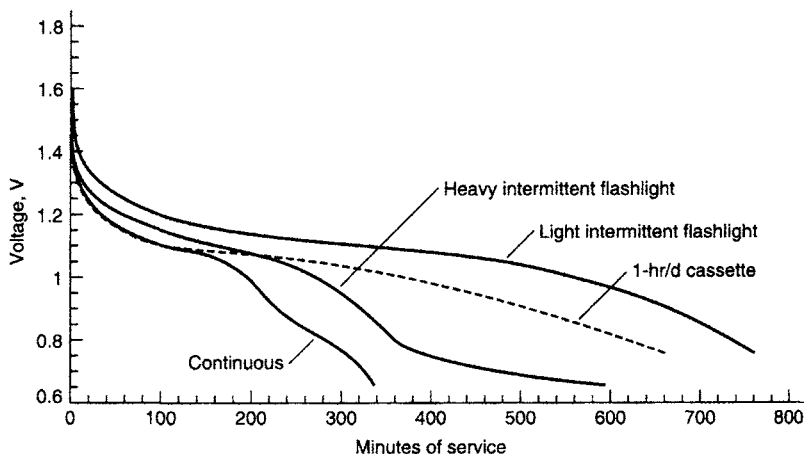


Figure 1.6. Examples of discharges in different conditions for a zinc-carbon battery. (From Ref. 6)

- **Storage and aging.** Even in a quiescent battery, reactions at the electrodes never stop, thus causing the so-called self-discharge. This is a parameter largely dependent on the cell chemistry and the storage conditions, *i.e.* state of charge and temperature. At higher storage temperatures, the capacity loss is faster. This may be reversible, but, in some cases, a permanent loss occurs. More generally, a battery experiencing operation (discharge or charge/discharge cycles) and storage periods, will age and lose performance. These concepts will be more extensively dealt with later.
- **Cell and battery design.** Cells may have these basic shapes: cylindrical, prismatic, coin (button). However, apart from the different sizes, cells with a given shape may differ in terms of internal construction. Examples are shown in Figure 1.7. As a function of the design, a cell may be suitable for long service life (high capacity) or for high rate applications. In the first case, illustrated by the bobbin type design of Figure 1.7d, there is a large amount of active materials. In the second (Figure 1.7c), the spirally wound configuration of thin electrodes enhances the surface area, thus allowing high currents and power. Ribbons of positive electrode, negative electrode and separator, bent in such a way to fill the space, characterize the prismatic design of Figure 1.7a. Alternatively, prismatic cells may have flat-plate electrodes, as is the case of lead-acid batteries. For a given shape, higher specific capacities and energies can be drawn as the cell size increases. Indeed, larger cells have a lower amount of inactive materials (case, contact, seals, *etc.*) with respect to the active ones.

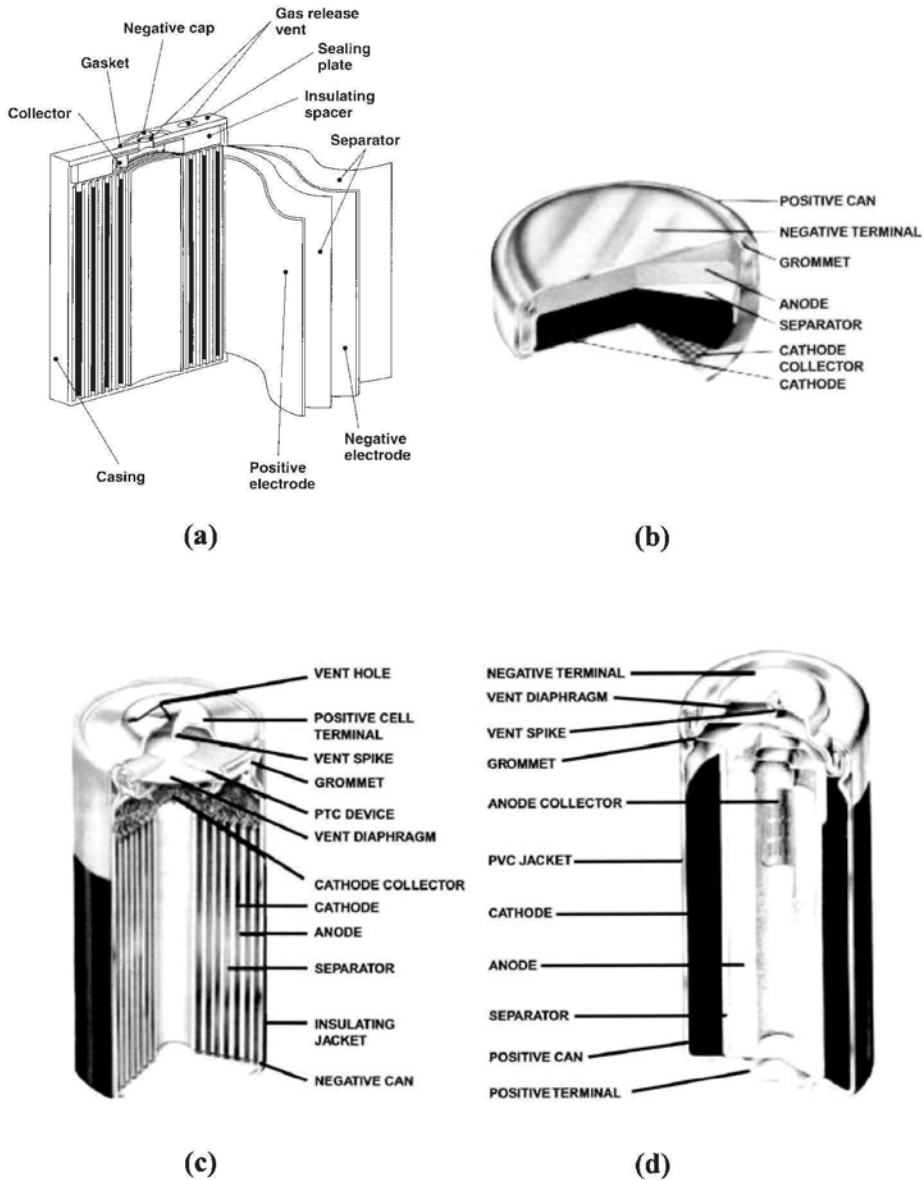


Figure 1.7. Examples of battery design: (a) prismatic (courtesy of Sanyo); (b) button; (c) spirally wound cylindrical; (d) bobbin type cylindrical. (The last three, from Ref. 7)

A multicell battery always has a lower performance than a single cell. This is not only due to additional weight brought about by proper cell

connection, insulation and electronic control, but also by possible cell unbalances and failures.

### 1.3.1. More Details on Cell Design

Cylinder is still the most used geometrical shape for cells, because of two fundamental advantages: ease of manufacture and mechanical stability. The latter point is especially important when a high internal pressure may develop either because of an abuse or because of the inherent characteristics of the systems. For instance, high pressures may develop in Ni-based cells (see later). A drawback of the cylindrical design is the space waste when cells are connected in a pack.

The prismatic configuration was introduced in the early 1990s to better use space in packs or in those applications, *e.g.* cellular phones, in which space is getting more and more limited. The prismatic design, now largely exploited especially in Li-ion cells, is more expensive than the cylindrical analogue, while the energy density is a bit lower. The first feature is explained by the fact that manufacturing is, as noted above, easier for the cylindrical design, while the second feature is due to lower amount of active material that can fill the prismatic shape. In terms of safety, the prismatic cell proves less resistant to an overpressure and tends to bulge. So far, there is no standardization of the prismatic sizes. The manufacturers, especially the ones also producing portable devices, tend to develop shapes and sizes suitable for specific applications.



Figure 1.8. Li-ion polymer pouch (or laminate) cell. (Courtesy of Sanyo)



The button (coin) cell design is mainly used in low-power applications, such as memory backup, watches and calculators. It is largely based on primary systems with Li or Zn anodes, but rechargeable cells (e.g. Li/MnO<sub>2</sub> and Li/Nb<sub>2</sub>O<sub>5</sub>) are also available (see Section 5.6). These small cells have no safety devices and the rechargeable ones can only be charged at low rates.

A cell design recently introduced is the so-called pouch (or laminate). In Figure 1.8, one such cell is shown. The pouch is made of a thin Al foil coated with a polymer film to isolate the electrodes. After assembling the cell, the pouch is thermally sealed, thanks to the melting of the polymer film. This design ensures light weight, flexibility and excellent space utilization in the device, with a packaging efficiency of 90-95%. This kind of cell case is prone to swelling if gas develops during operation. Furthermore, its resistance to mechanical abuses is obviously limited.

Thus far, not many details have been given on the electrode construction because of the large variety of techniques used as a function of the cell chemistry. Therefore, this aspect will be dealt with separately for each of the battery types presented in this book. Other practical aspects, such as separators,

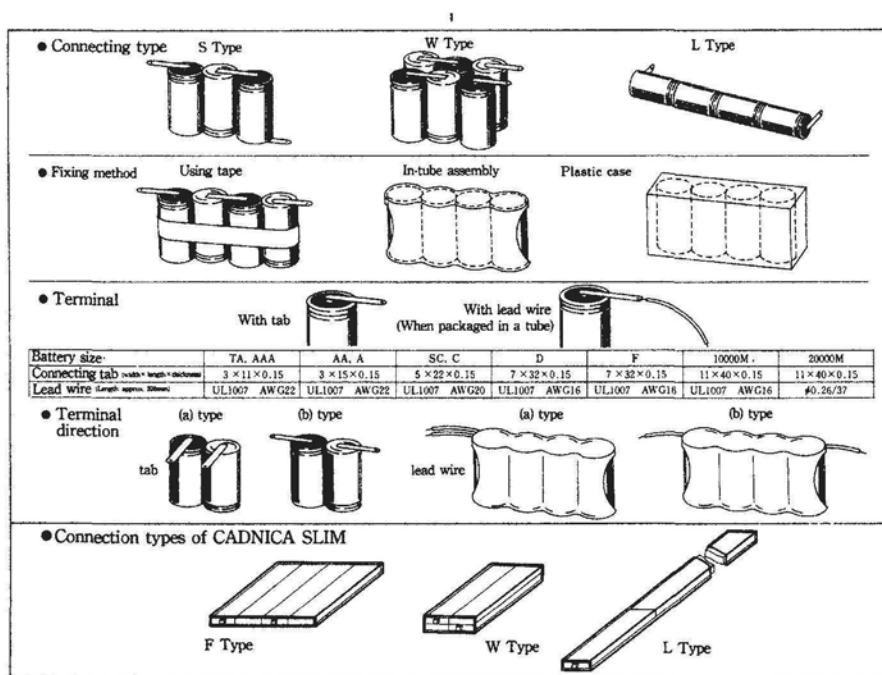


Figure 1.9. Connections of cells for nickel-cadmium (Ni-Cd) batteries. (Courtesy of Sanyo)

electrolytes, containers, connections, protection and management circuits, *etc.*, will be later detailed.

## 1.4. Cell Interconnections

The cells of Figure 1.7 and 1.8 can be connected to correspond to the requirements of a given device. In Figure 1.9, some examples of cell connections are shown for Ni-Cd cells. The same figure also shows how the cells can be fixed and the terminals attached. Nickel or nickel-plated steel tab connectors are mostly used through simple welding. They have sufficiently low resistivity, good mechanical properties and low tendency to form oxides at their surfaces. During welding, care must be taken not to damage the cell case. Excessive temperature might also damage the internal components.

In most cases, a series connection is made, which results in a battery voltage:  $V_{\text{batt}} = nV_{\text{cell}}$ , where  $n$  is the number of cell in series, while the battery capacity is just the same as the cell capacity. The series resistance is the sum of the resistances of the single cells (see also Appendix B), and this has to be taken into account in applications demanding high currents. In this respect, it is also important that the safety and management devices used in some cells (see Chapter 7) have a relatively low resistance. In any case, some IR losses through these devices are unavoidable.

Rechargeable cells in series call for the need of an accurate cell balance. If in a string of cells the charge voltage limit is not reached at the same time by all cells, their discharge/charge capacity will progressively diverge. This will ultimately result in malfunctions and safety problems. A proper cell management has to take into account cell balancing (Chapter 7).

In parallel cell connection, the voltage is the same of the individual cells, the total resistance is:  $1/R_{\text{tot}} = 1/R_1 + 1/R_2 + \dots 1/R_n$  (Appendix B) and the overall capacity is the sum of the single capacities. This kind of connection is often used with Li-ion cells.

Series/parallel connections are used to increase both the voltage and capacity.

As shown in Figure 1.7(a,c,d), some cells have a vent for gas releasing in case of internal overpressure. Accordingly, the multi-cell battery must allow escape of these gases, *e.g.* it has to have a pressure relief valve or a breathing mechanism.

The battery must also enable efficient heat dissipation when current is flowing through the cells. This point is especially critical when cells are in a plastic case (see Figure 1.9).

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## Chapter 2

# CHARACTERISTICS OF BATTERIES FOR PORTABLE DEVICES

## 2.1. Common Portable Electric and Electronic Devices and Their Batteries

The number of portable devices has experienced a dramatic growth. In particular, the devices forming the so-called 4 Cs, *i.e.* cellular phones, portable computers, camcorders and cordless power tools, have given a remarkable impulse to the market. The technological progresses in the field of semiconductors and other electronic components have played a very important role. However, this growth would have been impossible without the introduction of new batteries with improved performance.

Let us go for a while back to the 1940s-1950s. At that time, the portable applications were limited to torches, a few toys, and radios. Before the transistor's era, 'portable' radios used thermoionic valves that needed two types of batteries: a 2 V Pb-acid battery to supply current to the valve filament and a high V battery, consisting of up to 120 dry cells in series, to provide the voltage needed to accelerate electrons between the valve cathode and anode [1]. This radio weighed several kilograms and had to be maintained in an upright position to avoid acid spillage. Obviously, it was mainly used in military and industrial applications.

This sounds like a tale to people now accustomed to tiny devices powered by tiny cells. It has been calculated that today's family has 30-60 batteries in its portable appliances. If this number seems too high, just think about watches, cameras, camcorders, calculators, PDAs, cellular phones, notebook computers, radios, portable TVs, recorders, toys, electronic games, CD and DVD players. None of these devices would exist, at least in their present shapes and performance, if materials science and technology were unable to produce today's batteries.

Tables 2.1 and 2.2 summarize common portable devices and the type of battery mostly used. It can be noted that in some applications primary batteries are used, in some others both can be used and, finally, there are devices that can only be powered by secondary batteries. Until few years ago, portable devices only contained primary batteries. However, the development of small secondary batteries with high energy and power has remarkably changed

this scenario. Nowadays, the tendency is to use primaries in low power applications and secondaries when high current is requested. When both can be used, primary Li batteries can be best interchanged with all secondaries, by virtue of their good energy and power capability. The choice then mostly depends on cost considerations. A device which is not very often used can be

Table 2.1. Applications in portable devices, some typical currents, and use of primary or secondary batteries. (Adapted from Ref. 5)

Application		Current (mA)	Primary battery	Secondary battery <sup>1</sup>
<b>Light</b>	Lantern		Alkaline	
	Flashlight	100-700	Alk., Zn-Carbon	
	Penlight		Zn-Carbon	
	Keylight		Li/MnO <sub>2</sub>	
<b>Audio</b>	Headphone Stereo		Alkaline	Yes
	CD, MD Player	100-350	Alkaline	Yes
	Radio Cassette Player	70-200	Zn-Carbon	
	Handy Radio	70-200	Alk., Zn-Carbon	
<b>OA Instrument<sup>2</sup></b>	PDA		Li/MnO <sub>2</sub>	
	Calculator	<1	Alkaline, Silver <sup>3</sup>	
	Notebook	500-1500		Yes
	PC	800-1000		Yes
	Handy Terminal	400-800		Yes
<b>Communication</b>	Pager		Alkaline	
	Transceiver		Alkaline	Yes
<b>Movie</b>	Digital Still Camera	500-1600	Alkaline	
	Camera	200-1600	Alkaline	
	Video Recorder	700-1000		Yes
	LCD Television	10-25		Yes
<b>Watch</b>	Clock		Zn-Carbon	
	Watch	10-25	Silver <sup>3</sup>	
<b>Toy</b>	Electric Toy		Alkaline	
	Radio Control	600-1500	Alkaline	
	Electronic Game	20-250	Alk., Li-MnO <sub>2</sub>	
<b>Tester</b>			Alkaline, Silver <sup>3</sup>	

1. Mostly Li-ion batteries. 2. OA=Office Automation (see Appendix C for acronyms). 3. Zn/Ag<sub>2</sub>O batteries.

Table 2.2. Batteries used for memory backup of the corresponding applications. (From Ref. 5)

Application		Battery		
		Primary Li/MnO <sub>2</sub>	Secondary Li/MnO <sub>2</sub>	Li-ion
<b>Telecommunication</b>	Mobile Phone		○	○
	PHS		○	○
	Transceiver		○	○
<b>Information</b>	OA Machine (FAX, Printer)	○	○	
	Notebook	○		
	PC	○	○	
	PDA	○	○	○
	Handy Terminal	○	○	○
<b>Movie</b>	Video recorder	○	○	○
	Digital Camera	○	○	○
	Camera	○		
	LCD Television		○	○
<b>Audio</b>	Headphone Stereo	○	○	○
	CD Player	○	○	○
	MD Player	○	○	○
<b>Watch</b>		○		○
<b>Others</b>	Medical Instrument	○	○	
	FA Instrument	○	○	

better powered by a relatively cheap primary. In addition, such a battery has the advantage of a longer shelf-life. In Table 2.3, one can see at a glance for each battery: chemistry (electrodes and electrolyte), designation (see Chapter 3), voltage profile, advantages and main applications.

In Figure 2.1, the energy outputs on a gravimetric and volumetric basis are compared for several systems, while in Figure 2.2 the energy/current characteristics of primary and secondary batteries are presented. These figures

confirm that primary batteries feature higher energies than secondaries, but as the current demanded to the battery increases, the gap tends to reduce. In general, secondary batteries are better suited for high rate applications, as stated above. However, primaries based on Li, with proper construction characteristics, can deliver quite high energies even at relatively high current rates.

Another important parameter is the operating temperature range. As shown in Table 2.3 and in Figure 2.3, secondary batteries can be discharged down to  $-20/-40^{\circ}\text{C}$  with a limited penalty in their energies. Instead, the higher energies of the primary batteries are remarkably reduced at low temperatures.

Looking at Table 2.3, and Figures 2.1 and 2.3, one may note discrepancies as regards the energy outputs and the operating temperature range. This depends essentially on three factors: a) battery construction (even for a given chemistry); b) producer; c) discharging (and charging, when applicable) regime. Additionally, especially for Li and Li-ion systems, the evolution is so fast, that even a couple of years may have significance on the energy values reported. Later in this book, attempts will be done to correlate the

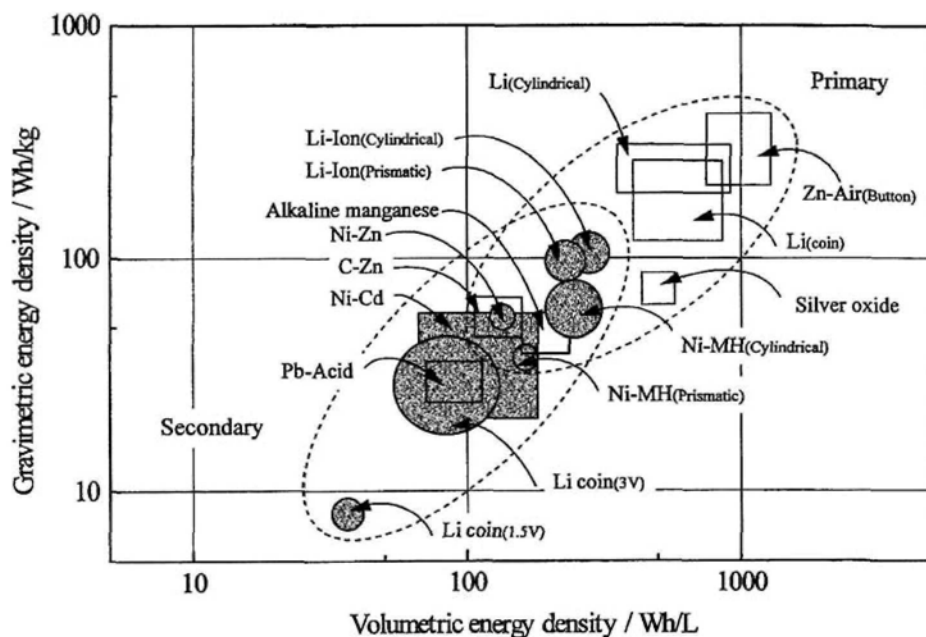


Figure 2.1. Gravimetric and volumetric energy density for primary and secondary batteries. (From Ref. 8)

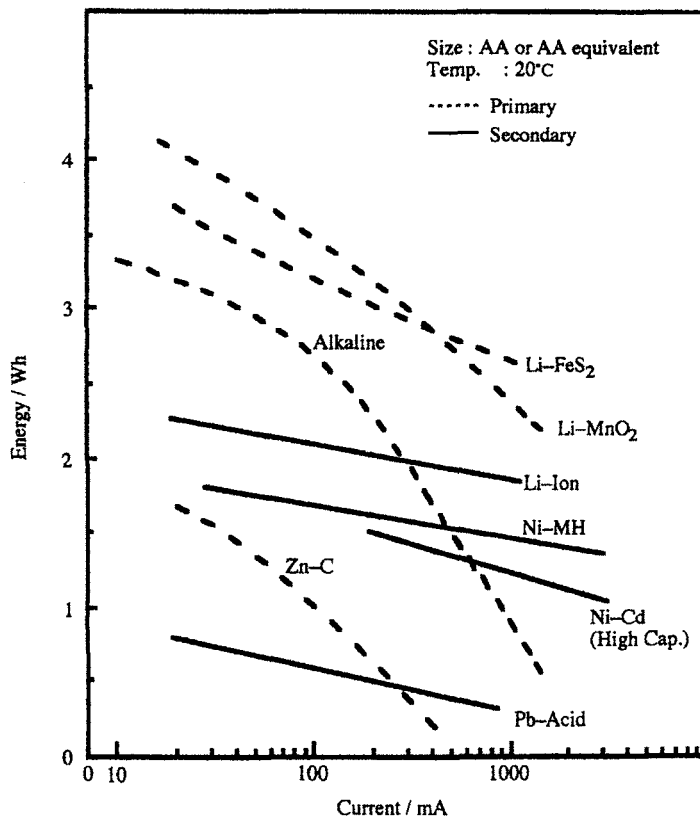


Figure 2.2. Energy output of cylindrical primary and secondary batteries as a function of the current requested. Batteries of the common AA size or equivalent (see Chapter 3). (From Ref. 8)

battery characteristics to more definite sizes and operating conditions.

In Figure 2.4, the shelf-life (or self-discharge) characteristics at various temperatures are presented. This figure confirms the superior capacity retention of all primaries even at high temperatures. Among the secondaries, the rechargeable alkaline MnO<sub>2</sub> (RAM) cell has about the same behavior of the primary with the same chemistry. Therefore, this is the secondary with the best charge retention, provided that it is fresh or fully recharged. Among the major secondaries, the Li-ion ones stand out, while Ni-Cd and Ni-MH have poor shelf-life characteristics. With the exception of RAM, all secondaries lose their total capacities in one year or less for storage temperatures above 50°C. Obviously, fully discharged secondaries may be recharged, but there are cases in which a fraction of the charge before storage is permanently lost.



If only self-discharge at room temperature (around 20°C) is considered, and taking into account that a battery is considered discharged if it cannot deliver at least 80% of its rated capacity, the following storage times may be indicated for some popular batteries. Zn-carbon: a couple of years; alkalines: five years; primary lithium: about ten years; Pb-acid: six months; Ni-Cd: about a month; Ni-MH: two-three weeks; rechargeable Li: several months.

## 2.2. Summarizing the Criteria of Choice of Primary and Secondary Batteries for Portable Devices

When buying a portable device, the user finds in most cases a battery included and, in the manual, its characteristics and instructions for proper use. In other words, the OEMs (Original Equipment Manufacturers) make a choice for a given device. This is normally a sensible choice, which, however, is based on general considerations: voltage, capacity, power (that is, current) and cost.

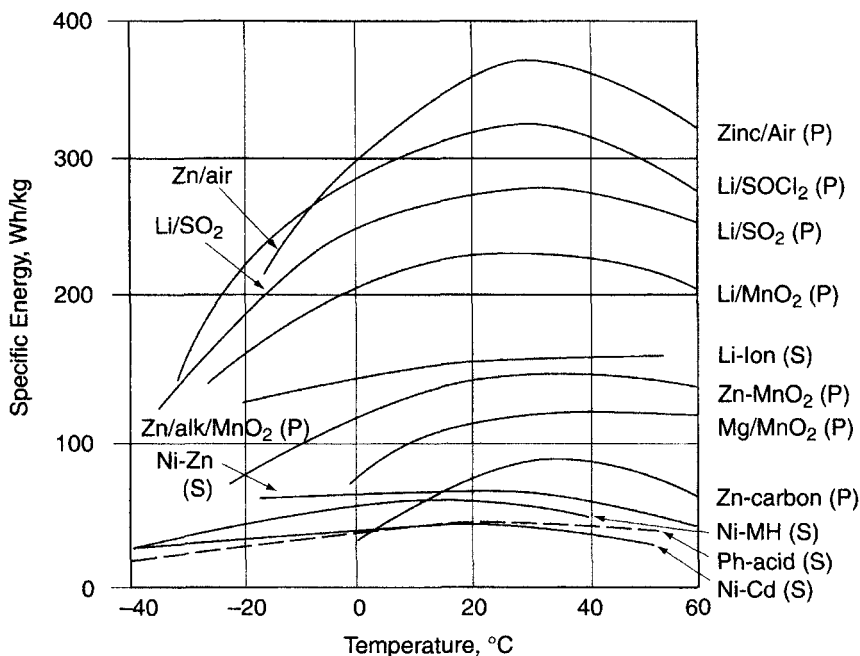
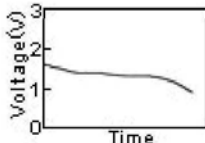
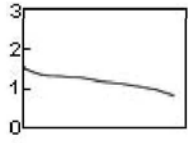
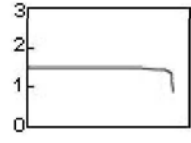
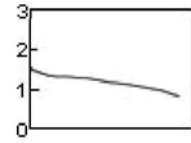


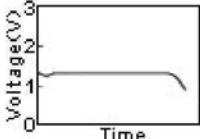
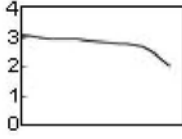
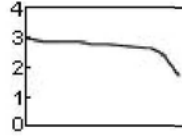
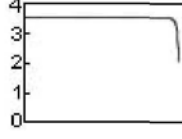
Figure 2.3. Effect of temperature on specific energy of primary and secondary batteries at the 20 hours rate. (From Ref. 9)

Table 2.3. Characteristics and applications of primary and secondary batteries for portable devices. (From Ref. 5)

Type	Manganese Dry Battery	Alkaline Manganese Battery	Silver Oxide Battery	Alkaline Button Battery
Designation	R	LR	SR	LR
Nominal Voltage <sup>+</sup>	1.5 V	1.5 V	1.55 V	1.5 V
Positive Electrode	Manganese Dioxide	Manganese Dioxide	Silver Oxide	Manganese Dioxide
Electrolyte Solution	Zinc Chloride	Potassium Hydroxide	*Sodium Hydroxide	Potassium Hydroxide
Negative Electrode	Zinc	Zinc	Zinc	Zinc
Discharge Characteristics				
Energy Density	Volumetric 150 Wh/L Gravimetric 70 Wh/kg	310 Wh/L 110 Wh/kg	450 Wh/L 120 Wh/kg	270 Wh/L 90 Wh/kg
Temp. Range	-10 to 55°C	-20 to 60°C	-10 to 60°C	-10 to 60°C
Strong Points	<ul style="list-style-type: none"> <li>•Wide Applications</li> <li>•Excellent Anti-leakage</li> <li>•No Hg, no Cd</li> </ul>	<ul style="list-style-type: none"> <li>•For Heavy and Continuous Use</li> <li>•High Reliability</li> <li>•No Hg, no Cd</li> </ul>	<ul style="list-style-type: none"> <li>•Flat Discharge Curve</li> <li>•Superior Long-term Reliability</li> <li>•High Energy Density</li> </ul>	<ul style="list-style-type: none"> <li>•Excellent Anti-leakage</li> <li>•Compatible with SR</li> <li>•Economical</li> </ul>
Applications	<ul style="list-style-type: none"> <li>•Radio Cassette Recorders</li> <li>•Headphone Stereos</li> <li>•Remote Controllers</li> <li>•Transceivers</li> <li>•Flashlights</li> <li>•Clocks</li> <li>•Calculators</li> </ul>	<ul style="list-style-type: none"> <li>•Cordless Phones</li> <li>•Headphone Stereos</li> <li>•CD Players</li> <li>•LCD TVs</li> <li>•Lanterns</li> <li>•Electric Shavers</li> <li>•Remote Controllers</li> </ul>	<ul style="list-style-type: none"> <li>•Wrist Watches</li> <li>•Cameras</li> </ul>	<ul style="list-style-type: none"> <li>•Toys</li> <li>•Wrist Watches</li> <li>•Portable Radios</li> <li>•Cameras</li> <li>•Electric Games</li> <li>•Measuring Instruments</li> <li>•Thermometers</li> </ul>

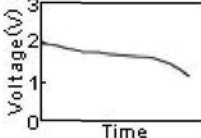
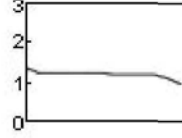

+ For definitions, see the glossary in Appendix D. \* Some silver oxide batteries have potassium hydroxide as electrolyte solution.

Table 2.3 (continued)

Type	Zinc Air Battery	Coin type Manganese Dioxide Lithium Battery	Wound type Manganese Dioxide Lithium Battery	Thionyl Chloride Lithium Battery
Designation	PR	CR	CR	ER
Nominal Voltage	1.4 V	3 V	3 V	3.6 V
Positive Electrode	Air	Manganese Dioxide	Manganese Dioxide	Thionyl Chloride
Electrolyte Solution	Potassium Hydroxide	Organic Electrolyte	Organic Electrolyte	Non aqueous Inorganic
Negative Electrode	Zinc	Lithium	Lithium	Lithium
Discharge Characteristics				
Energy Density	Volumetric 1150 Wh/L Gravimetric 390 Wh/kg	750 Wh/L* 260 Wh/kg*	670 Wh/L* 330 Wh/kg*	900 Wh/L 500 Wh/kg
Temp. Range	-10 to 60°C	-20 to 85°C	-40 to 60°C	-55 to 85°C
Strong Points	<ul style="list-style-type: none"> <li>•For Heavy and Continuous Use</li> <li>•Stable Discharge Curve</li> <li>•Excellent Anti-leakage</li> <li>•High Energy Density</li> </ul>	<ul style="list-style-type: none"> <li>•High 3V Voltage</li> <li>•Stable Discharge Curve</li> <li>•High Energy Density</li> <li>•Wide Usable Temperature</li> <li>•Superior Long-term Reliability</li> </ul>	<ul style="list-style-type: none"> <li>•For Heavy Duty Use</li> <li>•Wide Usable Temperature</li> <li>•Stable Discharge Curve</li> <li>•Low Self-discharge</li> <li>•Excellent Anti-leakage</li> </ul>	<ul style="list-style-type: none"> <li>•High 3.6V Voltage</li> <li>•Flat Discharge Curve</li> <li>•High Energy Density</li> <li>•Wide Usable Temp.</li> <li>•Super. Long-term Reliab.</li> </ul>
Applications	<ul style="list-style-type: none"> <li>•Hearing Aids</li> <li>•Pagers</li> </ul>	<ul style="list-style-type: none"> <li>•Memory Backup</li> <li>•Wrist Watches</li> <li>•PDAs</li> <li>•Electric Games</li> <li>•Cameras</li> <li>•Thermometers</li> </ul>	<ul style="list-style-type: none"> <li>•Cameras</li> <li>•Automatic Meter Reading</li> <li>•Measuring Instruments</li> </ul>	<ul style="list-style-type: none"> <li>•Memory Backup</li> <li>•Security/Alarm System</li> <li>•RF-ID Tag</li> <li>•Digital Set Top Boxes</li> <li>•Measuring Instruments</li> </ul>

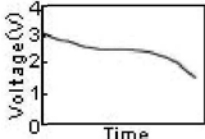
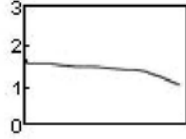
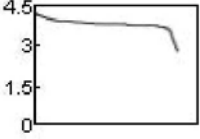
\* These values are above average and represent maximum performance for these cells. (Note of the author)

Table 2.3 (continued)

Type	Sealed Lead Acid Battery	Nickel-Cadmium Battery	Nickel-Metal Hydride Battery
Designation	—	—	—
Nominal Voltage	2 V	1.2 V	1.2 V
Positive Electrode	Lead Dioxide	Nickel Hydroxide	Nickel Hydroxide
Electrolyte Solution	Dilute Sulfuric acid	Potassium Hydroxide	Potassium Hydroxide
Negative Electrode	Lead	Cadmium	Hydrogen Absorbing Alloy
Discharge Characteristics			
Energy Density	Volumetric 100 Wh/L	100 Wh/L*	260 Wh/L
	Gravimetric 30 Wh/kg	30 Wh/kg*	80 Wh/kg
Temp. Range	-20 to 60°C	-20 to 60°C	-20 to 60°C
Strong Points	<ul style="list-style-type: none"> <li>•For Heavy Duty Use</li> <li>•Superior Long-term Reliability</li> <li>•Economical</li> <li>•Easy to recycle</li> </ul>	<ul style="list-style-type: none"> <li>•For Heavy Duty Use</li> <li>•High Mechanical Strength</li> <li>•High Efficiency Charge</li> <li>•Charge cycle: 500 times</li> <li>•Easy to recycle</li> </ul>	<ul style="list-style-type: none"> <li>•For Heavy Duty Use</li> <li>•No Heavy metal Use</li> <li>•High Capacity</li> <li>•Charge cycle: 500 times</li> </ul>
Applications	<ul style="list-style-type: none"> <li>•Portable AV Equipment</li> <li>•Lighting equipment</li> <li>•Power Tools</li> <li>•Medical Instruments</li> </ul>	<ul style="list-style-type: none"> <li>•Portable OA Equipment</li> <li>•Portable AV Equipment</li> <li>•Walkie-talkies</li> <li>•Power Tools</li> <li>•Medical Instruments</li> </ul>	<ul style="list-style-type: none"> <li>•Portable OA Equipment</li> <li>•Portable AV Equipment</li> <li>•Walkie-talkies</li> <li>•Power Tools</li> <li>•Medical Instruments</li> </ul>

\*These values are below average values from other sources (45 Wh/kg and 145 Wh/L). (Note of the author)

Table 2.3 (continued)

Type	Manganese Dioxide Lithium Rechargeable Battery	Titanium Lithium ion Battery	Lithium ion Battery
Designation	ML	TC	—
Nominal Voltage	3 V	1.5 V	3.7 V
Positive Electrode	Manganese Dioxide	Lithium Titanium Oxide	Lithium Cobalt Oxide
Electrolyte Solution	Organic Electrolyte	Organic Electrolyte	Organic Electrolyte
Negative Electrode	Lithium-Aluminum	Carbon	Carbon
Discharge Characteristics			
Energy Density			
Volumetric	160 Wh/L*	50 Wh/L	370 Wh/L
Gravimetric	54 Wh/kg*	18 Wh/kg	170 Wh/kg
Temp. Range	-20 to 60°C	-20 to 60°C	-20 to 60°C
Strong Points	<ul style="list-style-type: none"> <li>•For Back-up Use</li> <li>•Stable Discharge Curve</li> <li>•Excellent Anti-leakage</li> <li>•Long Life</li> </ul>	<ul style="list-style-type: none"> <li>•Excellent Cycle Performance</li> <li>•Wide Chargeable Voltage</li> <li>•Excellent Endurance for Overcharge</li> </ul>	<ul style="list-style-type: none"> <li>•For Heavy Duty Use</li> <li>•High 3.7V Voltage</li> <li>•No Memory Effect</li> <li>•Low Self-discharge</li> </ul>
Applications	<ul style="list-style-type: none"> <li>•Mobile Phones</li> <li>•Memory Backup for Notebook PCs</li> <li>•AV, OA Equipment</li> <li>•Wrist Watches</li> </ul>	<ul style="list-style-type: none"> <li>•Wrist Watches</li> <li>•PDAs</li> <li>•RTC Backup</li> <li>•Mobile Phones</li> </ul>	<ul style="list-style-type: none"> <li>•Portable OA Equipment</li> <li>•Portable AV Equipment</li> <li>•Radiotelegraphic Apparatus</li> <li>•Cameras</li> <li>•Electric Motorcars</li> </ul>

\*These values are below average values from other sources (120 Wh/kg and 265 Wh/L). (Note of the author)

The consumer can add considerations based on the operating conditions of his device. For instance, he may use it at high or low temperature, seldom or often, at continuous or intermittent regime, in a place where recharging facilities are available or in the wilderness, caring or not about cost. In addition to this, the consumer who gets himself up to date with technological advances may become aware that a newly developed and interchangeable battery has become available for his device. All this should make the consumer an active subject in the battery choice.

The battery characteristics described in this chapter may be a first aid. More data on the most common types of primary and secondary batteries will be given in the next chapters.

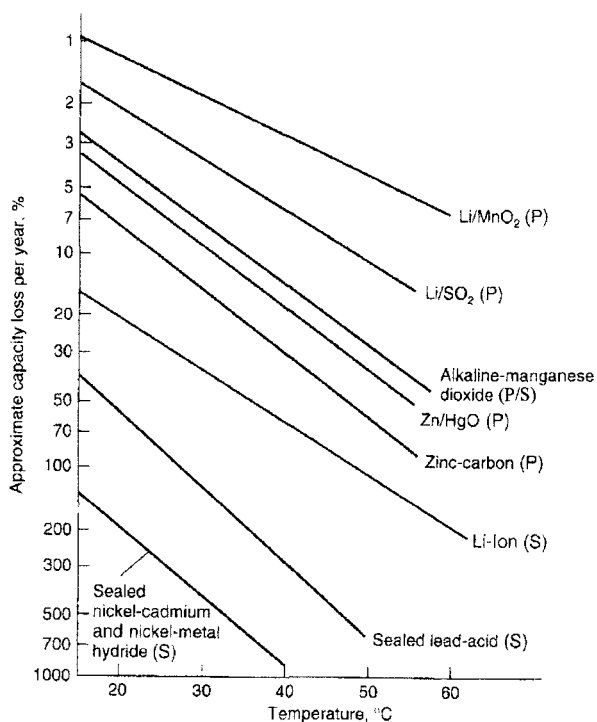


Figure 2.4. Shelf-life of primary and secondary batteries as a function of storage temperature. (From Ref. 10)

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## Chapter 3

# BATTERY STANDARDS AND SIZES

### 3.1. Designations of Primary Cells

The need of battery standardization was recognized early in the last century. Since then, several standards have been published by professional organizations and manufacturers. Today, the nomenclature created by the International Electrochemical Commission (IEC) is the most widely adopted.

Battery standards limit the number of battery types and allow their interchangeability if produced by different manufacturers. In Table 3.1, two methods proposed by IEC for designating primary cells are presented. Method 2 is more popular and easily connectible to cell dimensions and chemistry. The table also links a letter to a given electrochemical system. Examples of IEC nomenclature for primary round cells are provided in Table 3.2.

On the label of primary cells for the consumer marketplace, it is rather common to find the sizes expressed as AAA, AA, *etc.* In Table 3.3, these consumer designations are compared with the IEC designations and their average dimensions are given. Normally, the label also contains: 1) a specific code number identifying the producer; 2) the nominal voltage; 3) the cell expiration date (month/year); 4) the IEC designation; 5) safety warnings.

Examples of these warnings are:

- Do not dispose on fire
- Do not recharge
- Connect correctly (do not reverse polarity)
- Do not dissect
- Do not mix with used batteries or other battery types

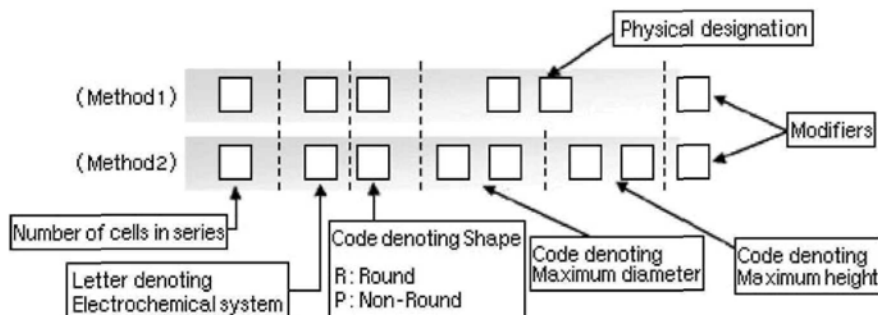
The safety issues will be later dealt with in detail.

### 3.2. Designation of Secondary Cells

Rechargeable batteries have received less attention in terms of standardization. Interchanging different primary cells is rather common for the consumer. For example, in an application requiring an AA 1.5 V cell, the consumer could use, according to Table 3.1, a zinc/carbon or an alkaline or a lithium/copper oxide cell. The same is not true for secondaries, as the tendency is to replace a battery with the same type and, often, the same brand. For



Table 3.1. Battery designation system for primary cells. (From Ref. 5)



Letter	Negative electrode	Electrolyte	Positive electrode	Nominal Voltage (V)	Maximum OCV(V)
-	Zinc	Zinc chloride	Manganese dioxide	1.5	1.72
B	Lithium	Organic electrolyte	Carbon monofluoride	3	3.7
C	Lithium	Organic electrolyte	Manganese dioxide	3	3.7
E	Lithium	Non-aqueous inorganic	Thionyl chloride	3.6	3.9
F	Lithium	Organic electrolyte	Iron disulfide	1.5	1.83
G	Lithium	Organic electrolyte	Copper oxide	1.5	2.3
L	Zinc	Alkali metal hydroxide	Manganese dioxide	1.5	1.65
P	Zinc	Alkali metal hydroxide	Oxygen	1.4	1.68
S	Zinc	Alkali metal hydroxide	Silver oxide	1.55	1.63

instance, the owner of a notebook powered by a Li-ion battery will not replace it with a Ni-MH.

In Table 3.4, the IEC designations for secondary cells are presented. It can be anticipated that the immediate success of the Li-ion battery, in the early 1990s, was due to the fact that a single cell could replace three cells in series with the Ni-Cd or Ni-MH chemistry - see the voltages - without the need of a revolution in terms of circuitry.

Table 3.2. Examples of IEC nomenclature for primary round cells.

IEC Designation	Number of Cells	System Letter	Shape	Dimensions (mm)		Description
				Diam.	Height	
R20	1	-	R	34.2	61.5	Cyl. Zn/Carbon
SR44	1	S	R	11.6	5.4	Cyl. Zn/Ag <sub>2</sub> O
LR44	1	L	R	11.6	5.4	Button alkaline
CR2032	1	C	R	20	32	Button Li/MnO <sub>2</sub>
ER17/50	1	L	R	17	52.6	Cyl. Li/SOCl <sub>2</sub>
2CR5	2	C	R	34 <sup>1</sup>	45 <sup>2</sup>	2 cyl. Li/MnO <sub>2</sub> in series

1, width; 2, height

Table 3.3. Common designation, IEC designation and dimensions of some primary alkaline batteries (all cylindrical, except the 9V battery).

Common Designation	IEC Designation	Diameter <sup>1</sup> (mm)	Height <sup>1</sup> (mm)
AAA	LR03	10.0	43.9
AA	LR6	14.0	49.8
C	LR14	25.5	49.2
D	LR20	33.2	60.5
N	LR1	12.0	30.2
9V	6LR61	47.5: 25.5: 16.5 (H:L:W) <sup>2</sup>	

1. Average values; 2. Prismatic battery

### 3.3. Performance Tests

The cell standardization started with the need of assessing the performance of primary cells and, as mentioned above, the concept was later modified to define mainly the size and chemistry. However, knowing the minimum performance of a cell in a given application is obviously important

Table 3.4. IEC nomenclature for secondary cells.

Letter	Negative electrode	Electrolyte	Positive electrode	Nominal Voltage (V)
H	Alloy	Aqueous alk.	Nickel oxide	1.2
K	Cadmium	Aqueous alk.	Nickel oxide	1.2
PB	Lead	Sulfuric acid	Lead dioxide	2
IC	Lithium	Organic electrolyte	Lithium Co oxide	3.8
IN	Lithium	Organic electrolyte	Lithium Ni oxide	3.8
IM	Lithium	Organic electrolyte	Lithium Mn oxide	3.8

and IEC has taken care to include these data in its standards. In Table 3.5, the results of typical IEC Application Tests for two R20 (D size) cells in different applications are reported.\*

Table 3.5. Results of Application Tests (IEC data) of standard Zn-carbon and alkaline cells (D size) in different applications.

Application	Standard Zn-carbon (R20) Minimum utilization time (hours)	Alkaline (LR 20)
Tape recorder <sup>1</sup>	4	25
Radio <sup>1</sup>	18	81
Toy <sup>1</sup>	2	15
Portable light <sup>2</sup>	0.5	7

1. Continuous use; 2. Intermittent use

---

\* In this book, for a battery designated by the chemical formula of the negative and positive electrode, *e.g.* Zn and MnO<sub>2</sub>, the notation with a slash will be used: Zn/MnO<sub>2</sub>. For a battery designated by a conventional definition, *e.g.* zinc carbon, the notation with a dash will be used: Zn-C.

## Chapter 4

# PRIMARY BATTERIES

### 4.1. Introduction

Primary batteries are still widely used in several portable applications (see Tables 2.1 and 2.3). They represent 80% of the total number of batteries sold. Their advantages are: no maintenance, availability in a large number of sizes, good shelf-life, high safety level, reliability and (for some types) low cost.

Up to the 1940s, the Zn-C system was the only one used for primary batteries. Since then, several other systems have been commercialized. One of them, based on HgO as a cathode, has been abandoned because of the environmental problems posed by mercury. Others, especially those based on the Li anode, have gained wide acceptance and contribute to their commercial success.

The consumers have also appreciated the continuous efforts aimed at improving the performance of primary batteries. In particular, energy, shelf-life and low-temperature operation have been brought to good levels. For instance, the common and cheap Zn-C cell (with  $\text{ZnCl}_2$  as electrolyte, see Section 4.2) has a specific energy of 85 Wh/kg, an energy density of 165 Wh/L, a lower operating temperature of  $-10^\circ\text{C}$  and a self-discharge of 7% per year at room temperature. Some types of Li cells (see Sub-sections 4.7.5 and 4.7.6) have specific energies  $>300$  Wh/kg, can work even at  $-60^\circ\text{C}$  and have shelf-lives in excess of 10 years.

These advances have been stimulated primarily by the growth of portable devices, with some contribution also given by space and military applications. The need of a cheap primary with a substantially higher energy than standard Zn-C has brought to the development of the alkaline Zn-C. Its specific energy is  $\sim 150$  Wh/kg and its energy density  $\sim 400$  Wh/L. At the same time, the Zn anode is now Hg-free, thus eliminating an important environmental problem. Furthermore, high power versions of the alkaline Zn-C are now available.

However, the most significant improvements have come from cells based on Zn/air and Li-anode systems. Their higher energy densities have allowed reduction of the battery size, thus making portable devices progressively smaller. Furthermore, these batteries have enough power density for use in demanding applications. On the other extreme, low-power applications (such as memory backup or medical electronics), which demand extreme reliability and very long shelf-life, have also taken advantage of these new chemistries.

## 4.2. Zinc-Carbon Batteries

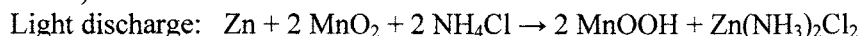
Georges Leclanché introduced the first Zn/MnO<sub>2</sub> battery in the middle of the 19<sup>th</sup> century. It contained a liquid electrolyte, which was later immobilized, thanks to Gassner, in an inert support. This is why the battery received the name of 'dry battery'. It is still largely used in moderate and light drain applications, as it is cheap and readily available. It cannot compete with alkaline Zn/MnO<sub>2</sub> in terms of performance, and its use is declining in the USA and Europe, while sales are still growing in emerging countries.

Dry batteries can use either the Leclanché or ZnCl<sub>2</sub> system. The former uses an electrolyte consisting of NH<sub>4</sub>Cl (26%) and ZnCl<sub>2</sub> (8.8%) in H<sub>2</sub>O (65%), while the latter contains ZnCl<sub>2</sub> (15-40%) in H<sub>2</sub>O (60-85%). Both contain inhibitors of Zn corrosion.

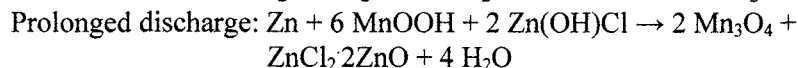
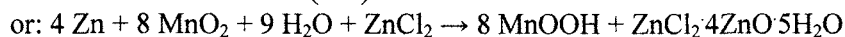
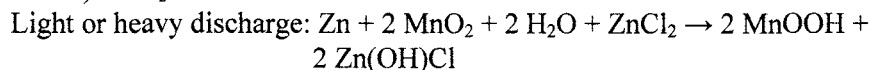
The electrodes are basically the same in both systems. The Zn can of the cell is also the anode, while a mix of electrochemically active MnO<sub>2</sub> and carbon is the cathode (Figure 4.1). In principle, the electrochemistry of the Zn-C cell is quite simple with Zn oxidation to Zn<sup>2+</sup> and MnO<sub>2</sub> reduction to the trivalent state for Mn (MnOOH or Mn<sub>2</sub>O<sub>3</sub>).

In practice, the reactions are rather complicated and depend on several factors, such as electrolyte concentration, temperature, rate and depth of discharge. Although still debated, the processes can be described as follows with a reasonable accuracy [11]:

### a) *Leclanché cell*



### b) *ZnCl<sub>2</sub> cell*



MnOOH is sometimes written as ½(Mn<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O). In the prolonged discharge, trivalent Mn is further reduced to Mn<sub>3</sub>O<sub>4</sub>, with an oxidation state of 2.67 for Mn. Mn<sub>3</sub>O<sub>4</sub> can also be written as MnO·Mn<sub>2</sub>O<sub>3</sub>. In typical applications, the reduction of MnO<sub>2</sub> is not continued beyond the formation of MnOOH.

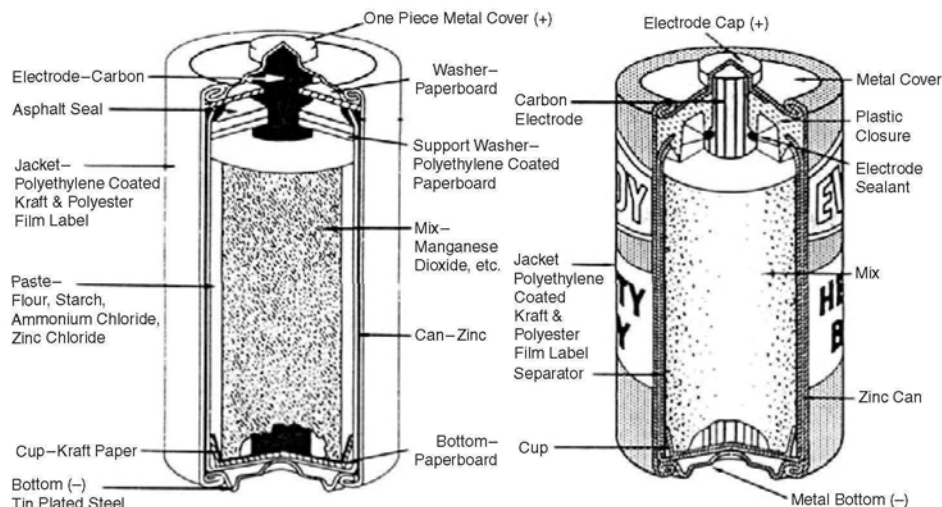


Figure 4.1. Standard (Leclanché, *left*) and heavy-duty ( $\text{ZnCl}_2$ , *right*) cylindrical Zn-C cells. (Courtesy of Energizer/Eveready)

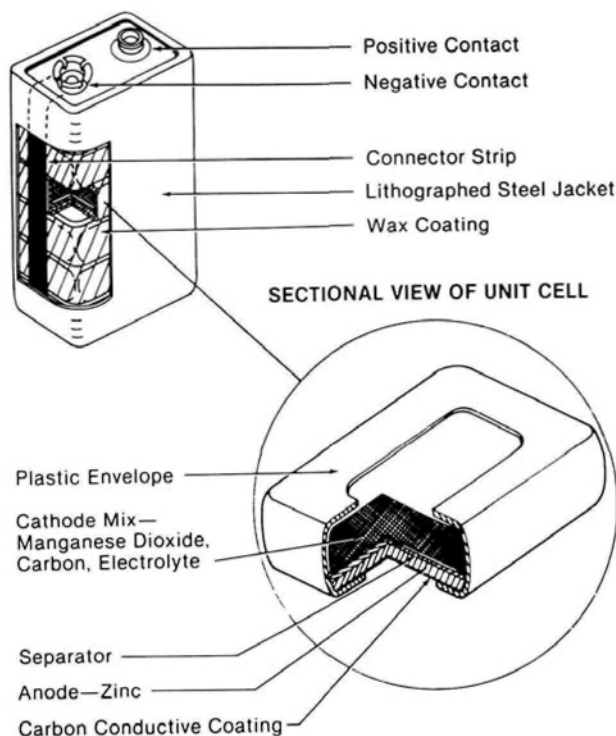
#### 4.2.1. Cell Construction and Materials

##### *Cylindrical configuration*

A bobbin containing a mix of  $\text{MnO}_2$ , carbon black and electrolyte surrounds the carbon rod, serving as a current collector for the cathode (Figure 4.1). The separator between the Zn can and the bobbin can be a paste of gelled flour and starch absorbing the electrolyte, or a paper thinly coated with the same paste. Paper-lined cells are now more widely used, also in view of the fact that the thinner separator leaves more space for the active materials. The Zn can was surrounded, in early cells, by a cardboard jacket. This had a serious drawback, as the can tends to become thinner because of the Zn oxidation to  $\text{Zn}^{2+}$ , and eventually may be perforated with electrolyte leaking. Therefore, the cardboard jacket has been replaced by a polymeric one, or by a polymer-coated steel container. In the Leclanché cell, the porous carbon rod also permits the escape of gases, which accumulate in the upper part of the cell. In the  $\text{ZnCl}_2$  cell, the escape of gases does not occur through the rod, which is sealed by wax, but through the plastic closure substituting the asphalt (see Figure 4.1). This improvement greatly limits  $\text{H}_2\text{O}$  loss and air intake.

##### *Flat Configuration*

Flat, rectangular cells can be stacked to give prismatic batteries of the type shown in Figure 4.2. The construction in this case is quite different from



**Figure 4.2.** Cutaway view of a flat Zn-C battery. (Courtesy of Energizer/Eveready)

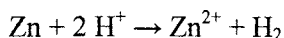
that of cylindrical cells. The Zn anode is coated with a carbon layer, so to act as an electron conductor for the cathode side of the cell. The  $\text{MnO}_2$ /carbon/electrolyte mix is separated from the Zn anode by a coated paper separator.

In these cells, the flat design provides more space to the cathode mix, so that the energy density is higher. The prismatic shape of the batteries, in turn, is more favourable to space saving: the volumetric energy density is twice that of a cylindrical battery. A typical prismatic battery is the popular 9 V. In this battery, six flat single cells are stacked in series. The positive pole directly contacts the cathode of the upper cell with a metallic cover, while the negative pole contacts the Zn anode of the bottom cell through a metal strip. The flat configuration is available in multi-cell batteries only (from four to several hundred cells in a stack or set of stacks).

The carbon black now used in the Zn-C cells is a special type, *e.g.* the highly porous acetylene black that remarkably increases the poor conductivity of  $\text{MnO}_2$  and holds the electrolyte. The use of this carbon has allowed doubling

the capacity with respect to cells containing graphite powder. Early cells contained naturally occurring  $\text{MnO}_2$  (NMD, usually pyrolusite) with a percentage of active material in the range 70-85%. Modern cells mostly use either chemical  $\text{MnO}_2$  (CMD) or electrolytic  $\text{MnO}_2$  (EMD), whose percentage of active material is 90-95% (the remainder is mostly  $\text{H}_2\text{O}$  plus several impurities). The use of synthetic  $\text{MnO}_2$  has allowed further doubling of the capacity with respect to cells using  $\text{MnO}_2$  from natural ore.

The Zn anode is ultrapure and used to be alloyed with Cd (~0.3%) and Pb (~0.6%) in order to improve its metallurgical properties and reduce corrosion. The legislation of several countries now prohibits the use of these toxic metals beyond a given (very low) limit, so that their content in modern cells is practically zero. Similarly, Hg used as the main corrosion inhibitor has been eliminated in cylindrical cells. Other materials now considered as inhibitors include: Ga, Sn, Bi, glycols or silicates. Zn corrosion is primarily due to the acidic character of both the  $\text{NH}_4\text{Cl}$  and the  $\text{ZnCl}_2$  solution (the latter being more acid):



The solution containing  $\text{ZnCl}_2$  is, anyway, preferable for a better performance. Indeed, formation of sparingly soluble Zn salts, which tend to accumulate near the electrode, greatly limits the ion diffusion in the Leclanché cell. With the  $\text{ZnCl}_2$  solution, this phenomenon is reduced, so that faster diffusion and enhanced rates of discharge are allowed. In other words, the electrode polarization, *i.e.* the cell potential drop under load, is lower in this solution.

In  $\text{ZnCl}_2$  cells, the  $\text{MnO}_2$ /carbon black ratio is lower to reduce cell resistance and allows higher currents. This ratio can vary from 3:1 to 11:1, but in some cells submitted to high pulse currents, a 1:1 ratio is used.

The better performance of the  $\text{ZnCl}_2$  cell, especially at high currents and moderately low temperature (down to  $-10^\circ\text{C}$ ), is counterbalanced by a higher cost. Overall, in terms of performance and cost, this cell lies between the common Leclanché and the alkaline cell. In Figure 4.3, D-size Leclanché and  $\text{ZnCl}_2$  cells of various grades are compared in intermittent discharge through a 3.9-ohm load [13]. The high rate (initial current:  $I=V/R=1.5/3.9=385 \text{ mA}$ ) enhances the difference between the two types of cells.

The rate of self-discharge of the  $\text{ZnCl}_2$  battery is lower than that of the Leclanché type. This is particularly evident when the construction differences are more marked. The former now uses starch-coated paper separator and molded plastic seals (Figure 4.1, right), while the latter, in its economical



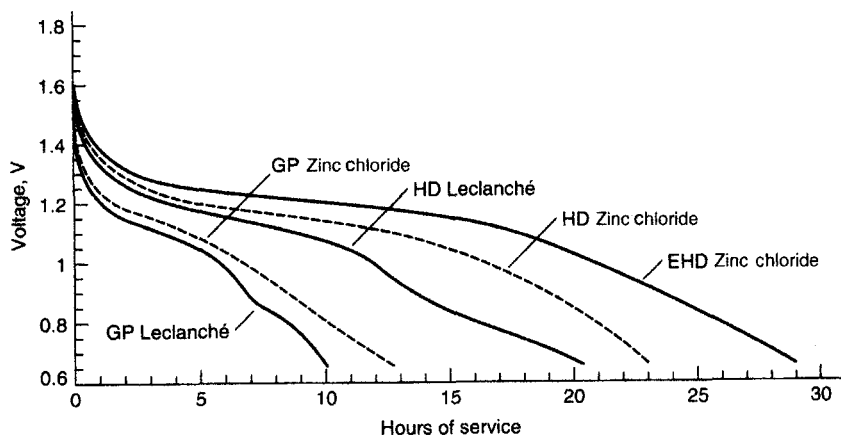


Figure 4.3. Discharge curves of D-size Leclanché and  $\text{ZnCl}_2$  cells on a simulated cassette application. Regime: 3.9 ohms, 1h/day at 20°C. GP, general purpose; HD, heavy duty; EHD, extra heavy duty. (From Ref. 13)

versions, uses starch type separator and asphalt seal (Figure 4.1, left). In summary, the characteristics of the two types of cells can be listed as follows [14].

*Leclanché cell:*

- Less expensive than alkaline or zinc chloride. Economical in terms of cost per hour of use on light current drains
- The widest variety of shapes, sizes, and capacities within the primary battery system. Available in voltages ranging from 1.5 volt to 510 volts
- Energy density of approximately 60-120 watt hours per liter
- Average service maintenance exceeds 90% after one year storage at 21°C on typical tests
- Lower specific energy than alkaline
- Sloping discharge curve
- Output capacity decreases as the drain rate increases
- Performance reduced at low temperatures
- Sensitive to changes in the discharge rate and/or use frequency

*Zinc Chloride cell:*

- Less expensive than alkaline. Economical in terms of cost per hour on moderate current drains or use frequency
- Less output capacity decrease than Leclanché as the drain rate increases
- Less sensitive than Leclanché to changes in the discharge rate and/or duty

cycle

- Lower internal resistance than Leclanché
- Better low temperature performance than Leclanché
- Energy density of approximately 120 to 150 watt hours per liter
- Average service maintenance exceeds 90% after one year storage at 21°C on typical tests
- Higher open circuit and initial closed circuit voltage than Leclanché or alkaline
- Lower specific energy than alkaline
- Available in voltages ranging from 1.5 volts to 12 volts and in a variety of shapes and sizes
- Sloping discharge curve

In Table 4.1, examples of commercially available Zn-C batteries are listed. As already mentioned, other batteries are preferably used in high-end devices. However, the Zn-C ones may still be used in less sophisticated applications (Tables 2.1 and 2.3).

### 4.3. Alkaline Batteries

In the early 1960s, the alkaline Zn/MnO<sub>2</sub> battery was introduced and became immediately preferable to the Zn-C battery because of several benefits [7]:

- Up to ten times the service life of regular zinc-carbon cells
- Long service life at continuous, high drain discharge
- No need for “rest periods”
- Low internal resistance
- Rugged, shock-resistant construction
- Cost-effective on a cost-per-hour-of-service basis
- Good low temperature performance
- Excellent leakage resistance
- Long shelf-life

The initial cost of the alkaline battery is higher than that of analogous Zn-C batteries. However, its service life is longer, so that if the cost-per-hour of usage is considered, especially at high drains and continuous discharge, the alkaline battery becomes cheaper. Its higher capacity and energy vs. the standard Zn-C battery is due to the use of high-grade anode and cathode, and of the more conductive alkaline electrolyte.

Table 4.1. Examples of Zinc-Carbon batteries. (Courtesy of Panasonic)

Model Number	Size	Type	V	Diameter Inch (mm)	Height Inch (mm)	Av. Wt. oz (g)
R03(UM-4N)	AAA	Extra Heavy Duty	1.5	.413 (10.49)	1.752 (44.50)	0.34 (9.7)
UM-3N	AA	Extra Heavy Duty	1.5	.571(14.50)	1.988 (50.50)	0.67 (19.0)
UM-3D	AA	Heavy Duty	1.5	.571 (14.50)	1.988 (50.50)	0.64 (18.0)
UM-3	AA	General Purpose	1.5	.571 (14.50)	1.988 (50.50)	0.53 (15.0)
UM-2N	C	Extra Heavy Duty	1.5	1.031 (26.19)	1.969 (50.00)	1.82 (51.5)
UM-2D	C	Heavy Duty	1.5	1.031 (26.19)	1.969 (50.00)	1.69 (48.0)
UM-2	C	General Purpose	1.5	1.031 (26.19)	1.969(50.00)	1.55 (44.0)
UM-1N	D	Extra Heavy Duty	1.5	1.339 (34.01)	2.421 (61.49)	3.53 (100.0)
UM-1D	D	Heavy Duty	1.5	1.339 (34.01)	2.421 (61.49)	3.46 (98.0)
UM-1	D	General Purpose	1.5	1.339 (34.01)	2.421(61.49)	3.12 (88.0)
UM-5N	N	Extra Heavy Duty	1.5	.472 (11.99)	1.189 (30.20)	0.23 (6.55)

Model Number	Type	V	L Inch (mm)	W Inch (mm)	D Inch (mm)	Wt. oz (g)
006PN (9V)	Extra Heavy Duty	9	1.909 (48.49)	1.043 (26.49)	0.689 (17.50)	1.34 (38.0)
006PD (9V)	Heavy Duty	9	1.909 (48.49)	1.043 (26.49)	0.689 (17.50)	1.34 (38.0)
006P (9V)	General Purpose	9	1.909 (48.49)	1.043 (26.49)	0.689 (17.50)	1.31 (37.0)

Label Color:

Extra Heavy Duty = Black, Heavy Duty = Red, General Purpose = Blue

### 4.3.1. Electrode Materials and Processes

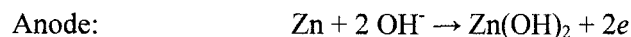
The anode of alkaline Zn/MnO<sub>2</sub> is essentially high-purity Zn powder. Its higher surface area vs. that of a Zn can affords higher discharge rates, while the electrolyte is more uniformly distributed. Furthermore, the combination of a porous anode and a conductive electrolyte reduces the extent of accumulation of reaction products near the electrode, this resulting in lower polarization. The practice of adding Hg, Pb or other heavy metals as gassing suppressors has been eliminated or greatly reduced. This has been made possible by a substantial reduction of the impurity level in the zinc powder, with particular reference to iron. A gelling agent is instead necessary for immobilizing the electrolyte and improving electrode processibility. To this end, starch, cellulose derivatives or polyacrylates are often used. The anode also contains the electrolyte, *i.e.* an aqueous KOH solution (35-52%), featuring higher conductivity and reduced gassing (Zn corrosion) in comparison with the acidic solutions used in Zn-C cells.

The cathode is based on electrolytic MnO<sub>2</sub> (EMD), as only this form can grant high power and long shelf-life. EMD contains ~92% MnO<sub>2</sub>, ~4.5 % H<sub>2</sub>O and several ionic impurities. The electronic conductor is carbon in the form of graphite, although some acetylene black may also be used to enhance the surface area. As for the anode, electrolyte is also added.

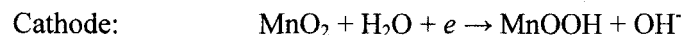
The separator, which has to be chemically stable in the concentrated alkaline solution, is normally a nonwoven fabric, as cellulose, vinyl polymer, polyolefin, or their combination.

The high porosity of cathode, anode and separator allows their saturation with the electrolyte. The homogeneous distribution and the high conductivity of the electrolyte afford high discharge rates also on continuous drains and at low temperatures.

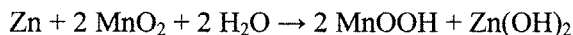
The electrochemical reactions occurring at the electrodes may be described as follows.



Due to the limited amount of water present at the anode, Zn(OH)<sub>2</sub> slowly loses H<sub>2</sub>O (Zn(OH)<sub>2</sub> → ZnO + H<sub>2</sub>O).



In this process, Mn<sup>IV</sup> is reduced to Mn<sup>III</sup> through the insertion of H<sup>+</sup> into the structure of electrolytic MnO<sub>2</sub>. The overall reaction in a discharge limited to the formation of MnOOH is:



In a prolonged discharge, the reduction of  $\text{MnO}_2$  proceeds to the formation of  $\text{Mn}_3\text{O}_4$ , as in the case of Zn-C cells. However, this reaction, to which a flat voltage-time curve corresponds, is seldom exploited.

Zn powder is obviously quite reactive and can decompose  $\text{H}_2\text{O}$  with the production of hydrogen. The latter can in turn cause  $\text{MnO}_2$  self-discharge, not to mention the overpressure it generates in the battery. As mentioned above, reducing the impurity level in the Zn powder greatly limits gassing. Otherwise, additives for the anode are necessary, such as ZnO (or other oxides) or organic inhibitors (polyethylene oxide compounds).

#### 4.3.2. Cell construction

The active materials of the alkaline cells are the same of the Zn-C cell (apart from the electrolyte). However, there are significant differences in the cell construction, which greatly contribute to its better performance.

##### *Cylindrical cell*

A cylindrical alkaline cell is shown in Figure 4.4. The can is not an active material, as in the Zn-C cell, but is made of steel or nickel-plated steel and acts as the cathode current collector. The cathode is pressed against the steel can by one of two processes: applying a high pressure to the powder when in contact with the can, or forming annular pellets, which are then inserted into the can. The Zn powder is allocated in the central cavity, around a brass current collector welded to the cell bottom (negative cap).

The anode cap is separated from the positive cell can by an insulator. A plastic grommet, sealed to the cell can, ensures that the cell is leak-proof. The grommet incorporates a membrane vent for relieving overpressure in case of short circuits or cell abuse.

##### *Button cell*

A button cell is shown in Figure 4.5. The Zn powder is in the upper part of the cell and contacts the negative cell top. A steel foil, usually having an external layer of nickel and an internal layer of Cu or Sn, makes the cell top. The can, acting as a container and cathode collector, is made of Ni-plated steel. It is insulated from the cell top by a plastic grommet over which is crimped to seal the cell. The  $\text{MnO}_2$  pellet, at the bottom of the cell, is covered by a separator and by an absorber for the electrolyte.

Table 4.2 lists cylindrical cells (together with some batteries), while Table 4.3 lists button cells. Thin prismatic alkaline batteries are also appearing in the

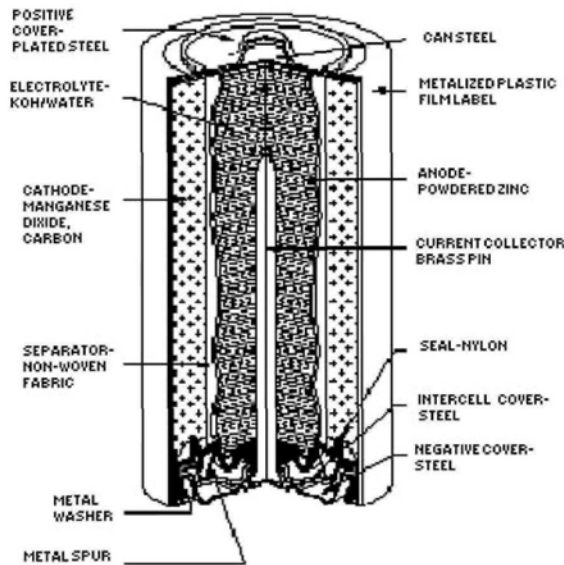


Figure 4.4. Cross section of a cylindrical alkaline cell. (Courtesy of Energizer/Eveready)

market, requested by compact digital audio (CDA) devices. New CD and CD/MP3 players are now 10 mm thick (vs. 20 mm for the old models) and require prismatic batteries with a thickness of ~6 mm.

#### 4.3.3. Cell Performance

Alkaline cells are compared in Figure 4.6 with analogous Zn-C cells under various loads. The log-log scale does not mask the differences between the two types of cells, especially for low discharge resistances.

This is also evident in Tables 4.4 and 4.5. As shown by the former, an alkaline cell lasts 4-9 times longer than its Zn-C analog.

Table 4.5 confirms these performance ratios, while stressing that the alkaline cell is cheaper than the Zn-C cell on a service-hour basis.

The alkaline cell also performs well in a wide temperature range (Figure 4.7). It can be noted that, while this cell could still be used at  $-20^{\circ}\text{C}$ , the Zn-C cell gives a very poor energy below  $0^{\circ}\text{C}$ . Furthermore, the energy of the Zn-C cell rapidly declines above  $40^{\circ}\text{C}$ .

The excellent rate capability even at low temperatures, the long shelf-life and the relatively low cost make the alkaline battery suitable for a variety of applications.

Table 4.2. Examples of standard alkaline cells (cylindrical, D to N) and batteries. (From Ref. 7)

PRODUCT NUMBER	SIZE	NOMINAL VOLTAGE	RATED CAPACITY*	LOAD	WEIGHT		VOLUME		TYPICAL GRAVIMETRIC ENERGY DENSITY**		TYPICAL VOLUMETRIC ENERGY DENSITY	
		volts	ampere-hours	ohms	pounds	kilograms	cubic inches	liters	watt-hours per pound	watt-hours per kilogram	watt hours per cubic inch	watt hours per liter
MN1300	D	1.5	15,000	10	0.304	0.138	3.440	0.056	59.2	130	5.2	322
MN1400	C	1.5	7,800	20	0.143	0.065	1.640	0.027	65.5	144	5.7	347
MN1500	AA	1.5	2,850	43	0.052	0.024	0.510	0.008	65.8	143	6.7	428
MN2400	AAA	1.5	1,150	75	0.024	0.011	0.230	0.004	57.5	126	6.0	345
MN9100	N	1.5	0,800	100	0.021	0.010	0.210	0.003	45.7	96	4.6	320
7K67	J	6.0	0.580	340	0.075	0.034	0.960	0.016	37.2	82	2.9	174
MN908	Lantern	6.0	11,500	15	1.349	0.612	30.620	0.502	40.9	90	1.8	110
MN918	Lantern	6.0	24,000	9	2.800	1.270	75.880	1.243	41.1	91	1.5	93
MN1604	9V	9.0	0.580	620	0.101	0.046	1.390	0.023	41.4	91	3.0	182

\* TO 0.8V per cell at 21°C (70°F).

\*\* Based on 1.2 volt average operating voltage per cell at 21°C (70°F).

Table 4.3. Examples of alkaline button cells. (From Ref. 5)

Model	Nominal Voltage (V)	Nominal Capacity (mAh)	Nominal Discharge Current (μA)	Diameter (mm)	Height (mm)	Weight (g)
LR44	1.5	60	100	11.6	5.4	1.8
LR43	1.5	55	100	11.6	4.2	1.6
LR1130	1.5	35	100	11.6	3.05	1.2
LR1120	1.5	26	45	11.6	2.05	0.9
LR41	1.5	25	70	7.9	3.6	0.6
4LR44	6.0	60	100	13.0	25.2	9.7

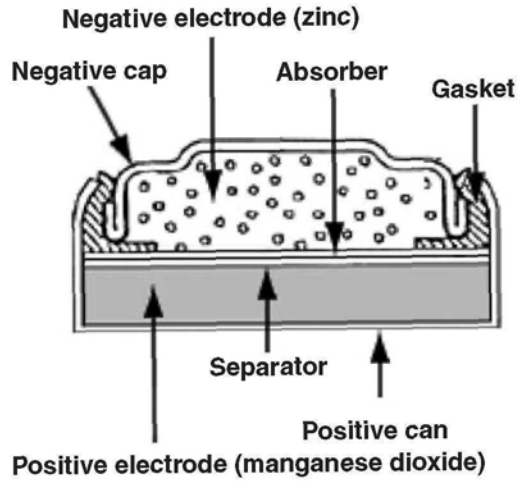


Figure 4.5. Cross section of a button alkaline cell. (From Ref. 5)

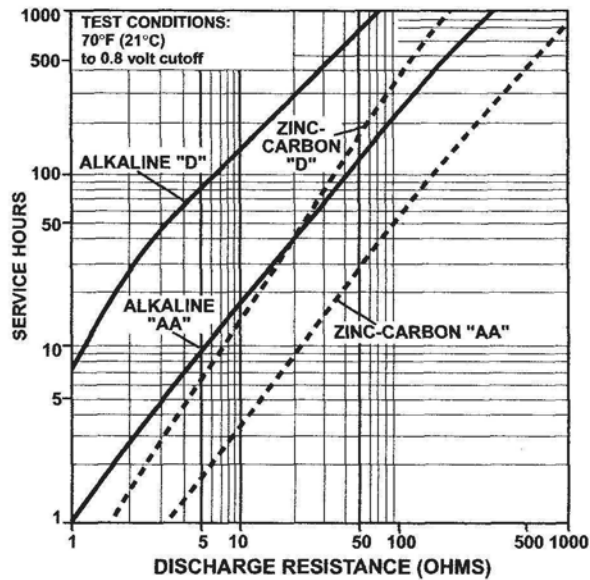


Figure 4.6. Comparison of AA- and D-size Zn-C and alkaline cells. (From Ref. 7)



Table 4.4. Ratio of the service time of an alkaline vs. a Zn-C cell in different applications. (From Ref. 14)

TEST	LOAD	DUTY CYCLE	E95 vs. 950* Typical Percent of Carbon Zinc Service
Motor Toy	2.2 ohms	1 hr/day	960%
Recorder	3.9 ohms	1 hr/day	440%
Flashlight	2.2 ohms	4 min/hr, 8 hrs/day	400%
Radio	39 ohms	4 hrs/day	425%

\* D-size batteries

Table 4.5. Service times of AA- and D-size alkaline and Zn-C cells in different applications, and relative costs (initial and per service hour). (From Ref. 7)

BATTERY TYPE	TEST*	ACTUAL SERVICE HOURS		RELATIVE COST PER SERVICE HOUR	
		ZINC-CARBON	ALKALINE	ZINC-CARBON	ALKALINE
D	Flashlight: 2.2 ohms	3.7	20.5	1	0.56
C	Toy: 3.9 ohms	2.2	20.8	1	0.33
AA	Flashlight: 3.9 ohms	1.1	6.2	1	0.41
AA	Tape Player: 10 ohms	3.5	17.4	1	0.47
	Relative Cost Ratios	0.35	1.0		

\* Test conditions: D - Flashlight - 2.2 ohms, 4 minutes/hour to 0.9 volts. C - Toy - 3.9 ohms, 1 hour/day to 0.8 volts. AA - Flashlight - 3.9 ohms, 4 minutes/hour to 0.9 volts. AA - Tape Player - 10 ohms, 1 hour/day to 0.9 volts.

A list of popular applications related to portable devices includes the following:

Heavy Duty Lighting	Transceivers
Camera Motor Drives	Electronic Games
Cassette Players and	Cellular Telephones
Recorders	Electronic Photoflashes
Shavers	Compact Disc Players
Portable Radios	Pagers
Portable TVs	Portable Computers
Motor Toys	Electronic Organizers
Clocks	(Video) Cameras

Several of these applications are now preferably powered by secondary batteries, and the alkaline ones are intended as an emergency replacement. However, it is interesting to note that these batteries could still be profitably used in the above devices if coupled to other power sources as supercapacitors (see page 221). Indeed, the latter could take care of current pulses, thus prolonging the life of the alkaline battery.

In 1999, premium alkaline cells have been commercialized. They are capable of even better performance at high discharge rates than the standard models. This has been made possible by a further reduction of the cell resistance through: coatings applied to both the negative and positive current collector; using a finer graphite grade; and, packing more  $\text{MnO}_2$  into the space available for the cathode. Coating reduces the build up of corrosion products on the current collectors, while a finer graphite powder improves the electronic conductivity.

A comparison of standard and premium alkaline cells in the digital camera test (1-A continuous drain) and the photo test (1-A pulses) is reported in Table 4.6. It can be noted that the premium cells tend to perform better, but not always. This depends on the brand and on the fact that the manufacturers are slowly improving the standard cells too for competitive reasons. There is indeed some confusion about that and consumer organizations often recommend buying alkaline batteries only by price.

#### **4.4. Zinc/Silver Oxide Batteries**

The Zn/silver oxide system provides a source of high energy with a rather flat potential. Furthermore, it performs well at low temperatures and has a good shelf-life. These characteristics make this system ideal for electronic devices requiring a small, high-capacity, long-lasting and constant-voltage cell. This

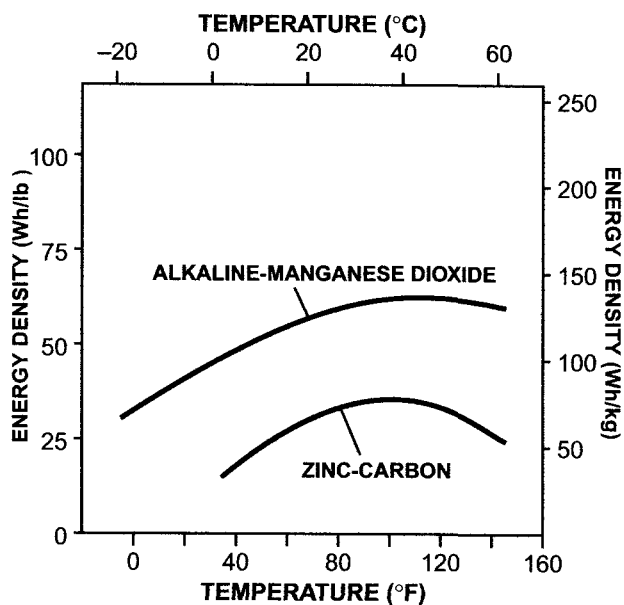


Figure 4.7. Comparison of the specific energies of alkaline and Zn-C cells in a wide temperature range. (From Ref. 7)

Table 4.6. Camera and photoflash tests for various alkaline R06 (AA) cells. (From Ref. 15)

Cell Type	Digital Camera <sup>1</sup> (min)	Digital Camera <sup>2</sup> (min)	Photo <sup>3</sup> (pulses)	Photo <sup>4</sup> (pulses)
Premium (Ultra) <sup>a</sup>	75	60	NA	NA
Premium (e2) <sup>b</sup>	50	40	528	330
Standard <sup>a</sup>	50	40	NA	NA
Standard <sup>b</sup>	50	35	432	300
Standard <sup>c</sup>	45	34	510	390
Standard <sup>d</sup>	55	40	NA	NA

Manufacturers: a) Duracell; b) Energizer; c) Rayovac; d) Panasonic

Regime: 1) 1 A, 0.9 V; 2) 1 A, 1 V; 3) 1 A, 10 sec/min, 1 h/d, 0.9 V; 4) 1 A, 10 sec/min, 1 h/d, 1.0 V.

system is mainly used in button cells (see a list in Table 4.7), while its use in larger batteries is limited by the high cost of silver.

The Zn/Ag<sub>2</sub>O cells were introduced in 1961 by Union Carbide as power sources for electronic watches. Their rated currents for this application range

from few microamperes for LCD watches to hundreds of microamperes for LED watches. These cells are also used in pocket calculators, hearing aids, cameras, instruments, reference voltage sources, *etc.*

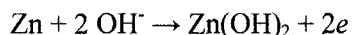
#### 4.4.1. Cell Materials and Electrode Reactions

The anode is zinc powder, the cathode is monovalent silver oxide,  $\text{Ag}_2\text{O}$ , and the electrolyte is a KOH or NaOH aqueous solution (20-45%).

##### *Zn Anode*

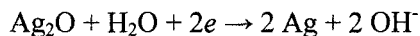
The Zn powder has to be highly pure, as already pointed out for alkaline  $\text{Zn/MnO}_2$ . Indeed, impurities (such as Cu, Fe, Sn) favour Zn corrosion and formation of  $\text{H}_2$ , thus producing an overpressure in the cell. In commercial cells, the Zn powder is amalgamated with Hg to keep corrosion under control. A low percentage of Hg is permitted. For instance, the European legislation (Commission Directive 98/101 of 22 Dec. 1998) allows mercury contents in these button cells up to 2% [16]. Gelling agents, such as polyacrylic acid and the like, are added to the anode to facilitate electrolyte accessibility.

The main anodic reaction is:

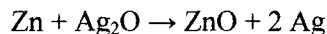


##### *Ag<sub>2</sub>O cathode*

The oxide of monovalent Ag is the only one now used in commercial cells. Unlike AgO, used until the early 1990s, it has a stable potential and does not need to be stabilized by heavy metals, as its reactivity with alkalis is low.  $\text{Ag}_2\text{O}$  is a poor semiconductor so that 1-5% graphite is added to have a satisfactory electronic conductivity. Furthermore, the reduction of  $\text{Ag}_2\text{O}$  produces Ag, which helps to reduce the cathode resistance. The cathode reaction is:



Therefore, the total cell reaction is (through the transformation of  $\text{Zn(OH)}_2$  into  $\text{ZnO}$ ):



The alkaline electrolyte contains some zincate to control gassing. KOH is preferred over NaOH in button cells submitted to high drains, as its conductivity is higher. NaOH is mainly used in cells for low-rate applications.

Table 4.7. Zn/Ag<sub>2</sub>O button cells. (From Ref. 5)

Model	Nominal Voltage (V)	Nominal Capacity (mAh)*	Nominal Discharge Current ( $\mu$ A)	Diameter (mm)	Height (mm)	Weight (g)	Applications
SR44W	1.55	165	200	11.6	5.4	2.2	High drain type
SR43W	1.55	125	200	11.6	4.2	1.8	
SR1130W	1.55	79	100	11.6	3.05	1.2	
SR1120W	1.55	55	100	11.6	2.05	1.0	
SR936W	1.55	75	100	9.5	3.6	1.1	
SR927W	1.55	57	100	9.5	2.73	0.8	
SR920W	1.55	39	100	9.5	2.05	0.6	
SR41W	1.55	39	50	7.9	3.6	0.7	
SR721W	1.55	25	50	7.9	2.1	0.45	
SR626W	1.55	28	50	6.8	2.6	0.4	
SR621W	1.55	18	50	6.8	2.15	0.3	
SR44SW	1.55	165	200	11.6	5.4	2.2	Low drain type
SR43SW	1.55	110	100	11.6	4.2	1.7	
SR1130SW	1.55	80	100	11.6	3.05	1.2	
SR1116SW	1.55	29	50	11.6	1.65	0.7	
SR936SW	1.55	70	100	9.5	3.6	1.1	
SR927SW	1.55	55	100	9.5	2.73	0.8	
SR920SW	1.55	39	50	9.5	2.05	0.6	
SR916SW	1.55	26.5	50	9.5	1.65	0.5	
SR41SW	1.55	45	50	7.9	3.6	0.7	
SR726SW	1.55	33	50	7.9	2.6	0.5	
SR721SW	1.55	25	30	7.9	2.1	0.45	
SR716SW	1.55	21	30	7.9	1.68	0.3	
SR712SW	1.55	10	20	7.9	1.29	0.25	
SR527SW	1.55	17	30	5.8	2.7	0.3	
SR521SW	1.55	14	20	5.8	2.15	0.2	
SR516SW	1.55	11.5	20	5.8	1.65	0.2	
SR512SW	1.55	5.5	5	5.8	1.25	0.14	
SR421SW	1.55	12	20	4.8	2.15	0.17	
SR416SW	1.55	8	10	4.8	1.65	0.12	
SR44	1.55	165	200	11.6	5.4	2.2	General type
SR1130	1.55	79	100	11.6	3.05	1.2	
SR1120	1.55	55	100	11.6	2.05	1.0	
SR41	1.55	39	50	7.9	3.6	0.7	
4SR44	6.2	160	200	13	25.2	11.7	

\*Nominal capacity indicates the duration until the battery voltage drops to 1.2 V when discharged at a nominal discharge current at 20° C.

#### 4.4.2. Cell Construction and Performance

The cell construction is similar to the one shown in Figure 4.5. The can containing the cathode and the cap containing the anode are made of the same materials cited for the button Zn/MnO<sub>2</sub> cell. As for the latter, the cell is anode limited, *i.e.* the anode capacity is 5-10% less than that of the cathode. This avoids Zn reaction with Ni or Fe of the cathode can, followed by H<sub>2</sub> generation.

A barrier of cellophane or grafted plastic membrane is set on top of the cathode pellet to prevent Ag<sup>+</sup> migration to the anode (Ag<sub>2</sub>O is slightly soluble in alkalis). A separator, usually fibrous polyvinyl alcohol, is added on top of the barrier to act as a further protection.

Typical discharge curves on constant loads and at room temperature are shown in Figure 4.8. The Zn/Ag<sub>2</sub>O cell performs well also at low temperatures if KOH is used. Indeed, cells with this electrolyte can work down to -28°C, while for those with NaOH the limiting temperature is -10°C.

In summary, the main characteristics of the Zn/Ag<sub>2</sub>O cell can be listed as follows [17]:

- Flatter discharge curve than alkaline manganese dioxide batteries
- Good low temperature characteristics
- Good resistance to shock, vibration, and acceleration
- Low and essentially constant internal resistance
- Excellent service maintenance: in excess of 90% after storage at 21°C for five years
- Available in voltages ranging from 1.5 to 6.0 volts and a variety of sizes.

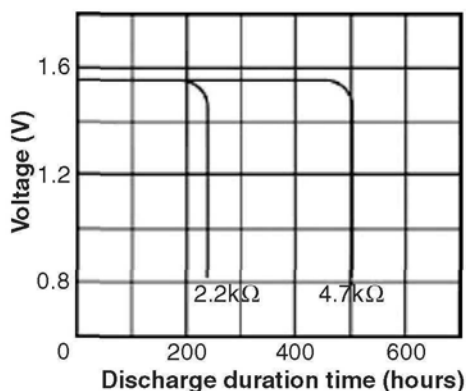


Figure 4.8. Continuous discharge curves of a Zn/Ag<sub>2</sub>O cell (rated capacity, 165 mAh) at room temperature. (From Ref. 5)

## 4.5. Zinc/Air Batteries

Zinc/air batteries, in their button form factor, are primarily designed to provide power to miniature hearing aids. In most hearing aid applications, these batteries can be directly substituted for Zn/Ag<sub>2</sub>O batteries and will typically give the longest hearing aid service of any common battery system.

Their general characteristics, also useful for other electronic devices, are [18]:

- Highest energy density for miniature batteries
- Relatively flat discharge curve (at 1.2-1.3 V)
- More stable voltage at high currents than silver oxide miniature batteries
- Essentially constant internal resistance
- Activated by removing covering (adhesive backed tab) from air access hole
- Constant capacity vs. load and temperature at standard drains
- Must have access to air (oxygen) to operate
- Excellent service maintenance prior to tab removal
- Low cost

Zn/air batteries use O<sub>2</sub> from the air as the active cathode material. O<sub>2</sub> diffuses through the cathode and, after reaching the cathode interface with the alkaline electrolyte, is catalytically reduced. In this respect, the cathode of the Zn/air cell resembles the one of a fuel cell. Moreover, since one active electrode material (O<sub>2</sub>) is outside the cell, the other (Zn) occupies most of the cell volume. This endows the cell with a high energy density (Wh/L). The capacity of the cell only depends on the anode, and, since the amount of Zn that can be stored in a given volume is about twice that of Zn/MnO<sub>2</sub> or Zn/Ag<sub>2</sub>O cells, the energy density of the Zn/air cell is very high (see Table 4.9).

### 4.5.1. Cell Materials and Construction

The anode is formed by high surface area Zn powder mixed with the electrolyte and, in some cases, a gelling agent. As Zn converts into ZnO during reduction, a volume increase ensues. Therefore, a portion of the volume occupied by the anode has to accommodate this expansion. The cathode region is quite complex (Figure 4.9): the holes allow air access; the air diffuser layer distributes O<sub>2</sub> uniformly over the cathode; the hydrophobic Teflon layer is O<sub>2</sub>-permeable but limits water vapor access; the air cathode is formed by a metallic mesh supporting the catalyst layer (carbon blended with Mn oxides and Teflon powder).

The rate at which O<sub>2</sub> enters and exits the cell depends not only on the holes area but also on the porosity of the diffuser membrane. In turn, the

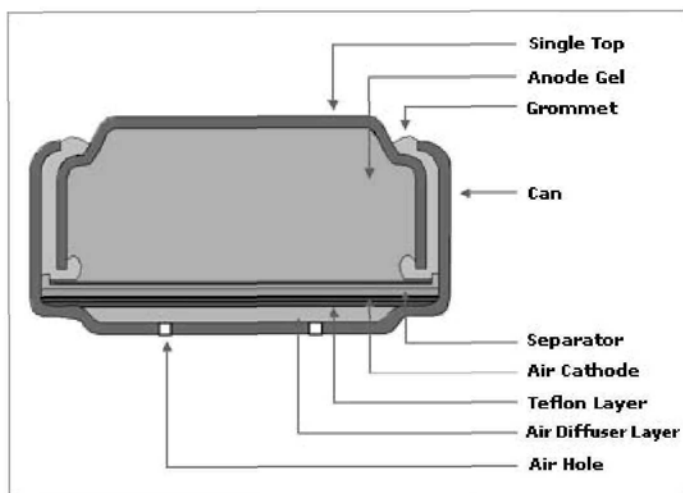
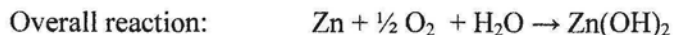
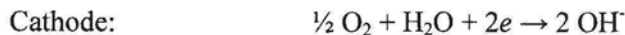
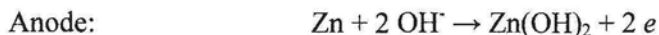


Figure 4.9. Cross-section of a button Zn/air cell. (From Ref. 19)

maximum current the cell can support depends on the  $O_2$  availability. Each Zn/air cell has its own limiting current. Cathode porosity and catalytic activity are critical in determining the real amount of  $O_2$  that can be reduced.

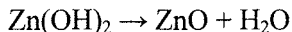
In principle, one is led to think that air access should not be regulated, so to have excess  $O_2$  and high discharge rates. In fact, strict regulation is necessary to limit the inlet of  $H_2O$  vapor and other gases which would degrade the cell. The electrolyte is typically a 30% KOH solution in water. In dry days, it tends to lose water, while the reverse occurs in wet days. In both cases, the service life of the cell is affected, this explaining why holes and diffusion membrane are necessary.

#### 4.5.2. Electrode Reactions

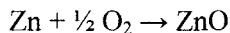


The hydroxide transforms into the oxide according to the reaction:





So, the overall reaction may be written as:



#### 4.5.3. Discharge Characteristics, Sizes and Applications

A typical discharge profile of the Zn/air cell is shown in figure 4.10. The potential remains fairly constant at discharge rates near the standard drains, even if the temperature is lowered down to 0°C. For instance, the cell of Figure 4.10 could be the 675 type (Table 4.8) having a capacity of 600 mAh and discharging at 2 mA (service life, 300 hours). However, at higher drains, the capacity delivered at 0°C remarkably decreases; for instance, it becomes 50% at the 75-h rate. As the electrolyte is a concentrated alkali solution, its viscosity increases at low temperatures, so reducing the ion mobility and the rate capability. On the other hand, service temperatures above ~50°C are not recommended, as the cells would lose rapidly H<sub>2</sub>O.

Standard sizes and rated capacities of button Zn/air cells are reported in Table 4.8. When used at the current drains of the table, these cells have operating lives of 1-3 months. These relatively short lives are not surprising if one considers that the cells are in contact with the atmosphere, and this

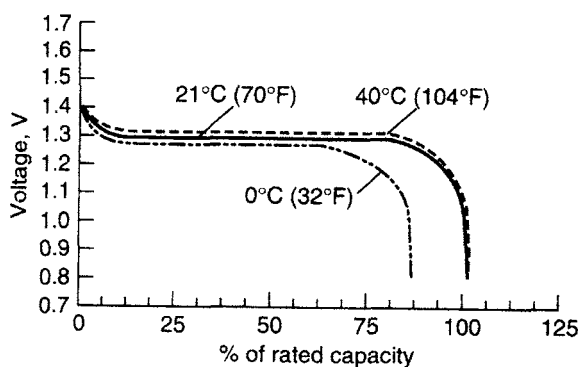


Figure 4.10. Discharge of a Zn/air cell at the 300-h rate and at different temperatures. (From Ref. 19)

Table 4.8. Characteristics of Zn/air button cells. Dimensions are IEC standards. (From Ref. 19)

Number	Diam. (mm)	Height (mm)	Weight (g)	Volume (cm <sup>3</sup> )	Capacity (mAh)	Drain (mA)
5	5.8	2.1	0.17	0.02	42	0.4
10	5.8	3.6	0.3	0.06	70	0.4
13	7.9	5.4	0.8	0.26	260	0.8
312	7.9	3.6	0.5	0.18	134	0.8
675	11.6	5.4	1.8	0.57	600	2

involves: direct Zn oxidation, carbonation of the electrolyte and gas transfer. So, they are better used in continuous applications or, anyway, when short non-operating times are expected.

Apart from hearing aids, the Zn/air cell can be used in the applications listed below [20]:

- Cardiac telemetry monitors (8.4 V battery)
- Bone growth stimulation (also with a multi-cell battery)
- Telecommunication receivers (pagers, e-mail devices, *etc.*)
- Telecom headsets using the Bluetooth wireless protocol.

A problem with this last application may be connected with the poor shelf-life of these cells (see above), as Bluetooth devices may not be used for weeks.

#### 4.6. Comparison of the Characteristics of Primary Aqueous Batteries

Table 4.9 reports all the aqueous primary systems discussed from Section 4.2 to Section 4.5. The table is self-explanatory and can help to identify, based on the reported performance and costs, the battery best suited for a given application.

#### 4.7. Lithium Batteries

Research on lithium batteries started in the 1960s and, after an unusually short lapse of time, gave birth in the 1970s to the first commercial products. However, these batteries were only used in niche applications, such as military and medical. Today, thanks to their high energy densities, long shelf-life and operation in a wide temperature range, primary Li batteries are used in several portable devices, such as cameras, watches, flashlights, calculators,

Table 4.9. Comparison of the main characteristics of aqueous primary cells. (Adapted from Ref. 21)

	<b>Leclanché (Zn/MnO<sub>2</sub>)</b>	<b>Zinc Chloride (Zn/MnO<sub>2</sub>)</b>	<b>Alkaline/Manganese Dioxide (Zn/MnO<sub>2</sub>)</b>	<b>Silver Oxide (Zn/Ag<sub>2</sub>O)</b>	<b>Zinc Air (Zn/O<sub>2</sub>)</b>
<b>System</b>	Zinc/Manganese Dioxide	Zinc/Manganese Dioxide	Zinc/Alkaline Manganese Dioxide	Zinc/Silver Oxide	Zinc/Oxygen
<b>Voltage Per Cell</b>	1.5	1.5	1.5	1.5	1.4
<b>Positive Electrode</b>	Manganese Dioxide	Manganese Dioxide	Manganese Dioxide	Monovalent Silver Oxide	Oxygen
<b>Electrolyte</b>	Aqueous solution of NH <sub>4</sub> Cl and ZnCl <sub>2</sub>	Aqueous solution of ZnCl <sub>2</sub> (may contain some NH <sub>4</sub> Cl)	Aqueous solution of KOH	Aqueous solution of KOH or NaOH	Aqueous solution of KOH
<b>Overall Reaction Equations</b>	$2\text{MnO}_2 + 2\text{NH}_4\text{Cl} + \text{Zn} \rightarrow \text{ZnCl}_2 \cdot 2\text{NH}_3 + \text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$	$8\text{MnO}_2 + 4\text{Zn} + \text{ZnCl}_2 \cdot 9\text{H}_2\text{O} \rightarrow 8\text{MnOOH} + \text{ZnCl}_2 \cdot 4\text{ZnO} \cdot 5\text{H}_2\text{O}$	$\text{Zn} + 2\text{MnO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 + 2\text{MnOOH}$	$\text{Zn} + \text{Ag}_2\text{O} \rightarrow \text{ZnO} + 2\text{Ag}$	$2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO}$
<b>Typical Commercial Service Capacities</b>	Several hundred mAh	Several hundred mAh to 38 Ah	30 mAh to 45 Ah	5 mAh to 190 mAh	30 mAh to 1,100 mAh
<b>Spec. Ener. (Wh/kg)*</b>	65 (cylindrical)	85 (cylindrical)	80 (button); 145 (cylindrical)	135 (button)	370 (button); 300 (prismatic)
<b>Ener. Dens. (Wh/L)*</b>	100 (cylindrical)	165 (cylindrical)	360 (button); 400 (cylindrical)	530 (button)	1300 (button); 800 (prismatic)
<b>Discharge Curve</b>	Sloping	Sloping	Sloping	Flat	Flat
<b>Temperature Range, Storage</b>	-40°C to 50°C	-40°C to 50°C	-40°C to 50°C	-40°C to 60°C	-40°C to 50°C
<b>Temperature Range, Operating</b>	-5°C to 55°C	-18°C to 55°C	-18°C to 55°C	-10°C to 55°C	-10°C to 55°C
<b>Effect of Temperature on Service Capacity</b>	Poor low temperature	Good low temperature relative to Leclanché	Good low Temperature	Low temperature depends upon construction	Good low temperature
<b>Internal Resistance</b>	Moderate	Low	Very Low	Low	Low
<b>Gassing</b>	Medium	Higher than Leclanché	Low	Very Low	Very Low
<b>Cost, Initial</b>	Low	Low to Medium	Medium Plus	High	High
<b>Cost, Operating</b>	Low	Low to Medium	Low to High	High	High
<b>% Capacity Loss per year @ 0°C</b>	3%	2%	1%	1%	NA
<b>% Capacity Loss per year @ 20°C</b>	6%	5%	3%	3%	5% (Sealed)
<b>% Capacity Loss per year @ 40°C</b>	20%	16%	8%	7%	NA

\*The original values representing energy ranges have been substituted by average values. (Note of the author)

measuring instruments, *etc.* However, because of their cost and safety issues (both decreasing), these batteries still lag behind, in terms of market shares, to the traditional Zn-anode primary batteries.

Batteries based on Li anode have attracted the attention of researchers due to the very high specific capacity and standard reduction potential of this element (3860 Ah/kg *vs.* 820 Ah/kg for Zn, and -3.0 V *vs.* -1.25 V for Zn [values for Li in organic solutions and for Zn in alkaline solutions]).

The combination of a high capacity with a high potential lends to the Li electrode an exceedingly high specific energy. However, Li is extremely reactive: not only is thermodynamically unstable in protic solvents such as H<sub>2</sub>O, but also in organic aprotic solvents. However, in some of them, such as propylene carbonate (PC) and butyrolactone (BL), Li is kinetically stabilized by the formation of a film preventing further reactions on open circuit.

From 1970 until the mid-1980s, significant progresses in understanding the processes occurring in Li cells have favored the development and commercialization of several primary batteries. A key point was the introduction of electrolytes with sufficiently high conductivity and, at the same time, able to form a stable protecting film on Li (the so-called solid electrolyte interface, SEI). Furthermore, as cathodes with more positive potentials, hence higher oxidation power, were introduced, the electrolytes had also to prove stable to decomposition by oxidation.

Several salts were investigated. Their first prerequisite was a sufficient solubility in the organic solvents used, so to have a good conductivity. Such salts include: LiClO<sub>4</sub>, LiAsF<sub>6</sub>, LiPF<sub>6</sub>, LiBF<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, *etc.* The first may create safety concern, while the second is both environmentally unfriendly and responsible for the instability (through polymerization) of the cyclic carbonates used as solvents [22].

Solvents now preferred include a combination of high-dielectric constant molecules (PC, ethylene carbonate [EC], *etc.*) and low-viscosity molecules (dimethyl carbonate [DMC], dimethoxyethane [DME], *etc.*). This combination grants a sufficient conductivity, a good SEI on Li, a wide liquid range *vs.* temperature, and a good electrochemical and thermal stability.

The basic characteristics making primary Li batteries well suitable for portable devices are:

- High energy (over 200 Wh/kg and 400 Wh/L)
- High (~3 V) and flat potential (with the exception of the Li/FeS<sub>2</sub> cell)
- Long shelf-life: ~1%/year at room temperature
- Wide temperature range: some cells may still work at -40°C and, for those with soluble cathodes (see below), this limit may be extended to -60°C

- Construction in several form factors: coin (button), cylindrical, prismatic and very thin (film or paper batteries with thicknesses of few hundred microns)

#### **4.7.1. Classification of Primary Lithium Batteries**

Li primary cells may be divided into three main types:

- Liquid or soluble cathode cells
- Solid cathode cells
- Solid electrolyte cells

The best example of a soluble cathode is  $\text{SO}_2$ , which dissolves in the electrolyte. Liquid cathodes, as  $\text{SOCl}_2$  (thionyl chloride) or  $\text{SO}_2\text{Cl}_2$  (sulphuryl chloride) also act, at the same time, as solvents for convenient salts. These cells can work thanks to the formation of a passive film on the Li anode. They can be manufactured in a wide variety of designs and capacities. Some designs allow very high rates, this resulting in the highest power density of all primary cells.

Solid cathode cells are the most widely used in electronics and are based on such cathodes as  $\text{MnO}_2$ ,  $\text{CF}_x$ ,  $\text{FeS}_2$ ,  $\text{AgV}_4\text{O}_{11}$ , and  $\text{CuO}$ . They are normally used in low to medium rate applications, but some designs allow fairly high rate capabilities.

An example of solid electrolyte is  $\text{LiI}$  present in the first implantable battery,  $\text{Li/I}_2$ . A film of  $\text{LiI}$  is formed as soon as the two electrode materials come into contact. These cells may have shelf-life of up to 20 years, and deliver currents in the microampere range.

In the next sub-sections, these cells will be described in details:  $\text{Li/SO}_2$ ,  $\text{Li/SOCl}_2$ ,  $\text{Li/MnO}_2$ ,  $\text{Li/CF}_x$ , and  $\text{Li/FeS}_2$ . Cells for medical applications,  $\text{Li/I}_2$  and  $\text{Li/AgV}_4\text{O}_{11}$ , will be dealt with in Chapter 6.

#### **4.7.2. $\text{Li/MnO}_2$ Batteries**

Commercialized since 1975, this primary Li battery is by far the most widely used (see Table 4.13). It has all of the nice features typical of Li batteries: high voltage, high energy (both on a gravimetric and a volumetric basis), wide operating temperature range, good power (in some designs), long shelf-life, safety, and low cost. The  $\text{Li/MnO}_2$  battery is produced by several manufacturers in coin, cylindrical or prismatic forms and can be used in a variety of applications.

#### 4.7.2.1. Materials and Electrode Reactions

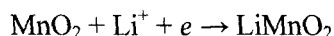
The Li/MnO<sub>2</sub> system was one of the first investigated by researchers working in this field and proved initially rather poor in performance. Substantial improvements had to be made with the organic electrolyte and the MnO<sub>2</sub> cathode to have the excellent cell available today.

The anode is lithium foil. Studies by Sanyo's researchers have demonstrated that Li-Al alloys, with a limited amount of Al, can improve the capacity retention on storage, while a too high Al concentration causes a lowering of the discharge voltage [23]. The cathode is electrolytic MnO<sub>2</sub>, which is used after a thermal treatment. This treatment, which causes H<sub>2</sub>O loss, rearrangement of the MnO<sub>2</sub> crystal structure and reduction of its surface area, provides this material with satisfactory electrochemical features.

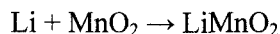
The nature of the electrolyte used in commercial batteries is not always disclosed. In Sanyo's batteries, LiClO<sub>4</sub> or LiCF<sub>3</sub>SO<sub>3</sub> (Li trifluoromethane sulfonate) are widely employed as solutes, and PC-DME (dimethoxyethane) as binary solvent mixture. The LiClO<sub>4</sub>-PC-DME electrolyte has a high conductivity [24].

An efficient electrolyte for low-temperature applications is obtained dissolving LiCF<sub>3</sub>SO<sub>3</sub> in a ternary solvent mixture: EC, butylene carbonate (BC) and DME. This electrolyte gives high capacities at low temperatures, but also on storage at high temperatures, *e.g.* 60°C. It features high conductivity and low viscosity [23].

The anodic reaction is Li oxidation ( $\text{Li} \rightarrow \text{Li}^+ + e$ ), while in the cathodic reaction Mn<sup>IV</sup> is reduced to Mn<sup>III</sup>. This happens as a consequence of the Li<sup>+</sup> insertion into the tunnels present in the MnO<sub>2</sub> crystalline structure:



The overall reaction is (see also Figure 1.2):



The above overall reaction corresponds to full discharge: one Li<sup>+</sup> is inserted into one MnO<sub>2</sub> molecule. Intermediate discharge states are best described by the formula Li<sub>*x*</sub>MnO<sub>2</sub>, with 0 < *x* < 1, which best explains the gradual accommodation of the Li<sup>+</sup> ions into the tunnels of the host structure.

#### **4.7.2.2. Cell Construction and Performance**

Li/MnO<sub>2</sub> cells are manufactured in the following designs: coin, spirally wound cylindrical, and bobbin type cylindrical (Table 4.10). All of them satisfy the requirement of portable devices. Examples of coin, spirally wound cylindrical and bobbin type cylindrical cells are shown in Figure 4.11.

In this figure, schematic cross sections of these cells are reported to emphasize the construction details, with particular reference to the differences in the cylindrical cells as regards crimp- or laser-sealing. In Figure 4.11a, the pellet of MnO<sub>2</sub> and carbon (the latter increases the poor electronic conductivity of the oxide) is allocated at the bottom of the cell and separated from the Li anode by a nonwoven polypropylene separator wet by the electrolyte. In the bobbin structure (Figure 4.11b), the amount of cathode is maximized to have high capacity and energy. Because of this structure, the cathode surface area is reduced and these cells can only be used at low drains. Sealing is made through laser welding to ensure perfect isolation and long shelf-life (up to 10 years at room temperature).

In the spirally wound structure (Figure 4.11c,d), a thin layer of the cathode mix is supported on a metal grid. Three strips, Li foil, separator, and cathode, are tightly wound to form a high surface area structure capable of sustaining high currents. There are significant construction differences between the cell with crimp sealing and the one with laser sealing. In particular, in the former, the can is negative, while in the latter the can is positive. The same inversion has been made for the alkaline vs. the Zn-C cell (see Sections 4.2 and 4.3).

In Figure 4.12a,b, the discharge characteristics of spirally wound and bobbin cylindrical cells are shown as a function of temperature. The former can still deliver a satisfactory capacity down to -40°C and is allowed to work up to 85°C. The wide liquid range of the electrolyte and the thermal stability of all cell components permit this performance. The high capacity bobbin cell discharged at low rates (in the microampere range) can operate for several years with minimum performance variations vs. temperature. Finally, Figure 4.12c stresses the excellent shelf-life of both button and cylindrical cells. After storage periods of 7-10 years at room temperature, 95% of the rated capacity could still be recovered upon discharge at standard rates (see Table 4.10).

The characteristics of various coin and cylindrical cells are shown in Table 4.10. In particular, the high rate capability of the spirally wound cells can be noted.

They can be submitted to continuous discharge at the C rate or to pulse discharge at rates above 2 C. The bobbin cells can be discharged at standard currents 5-10 times lower than those of the corresponding spirally wound cells.

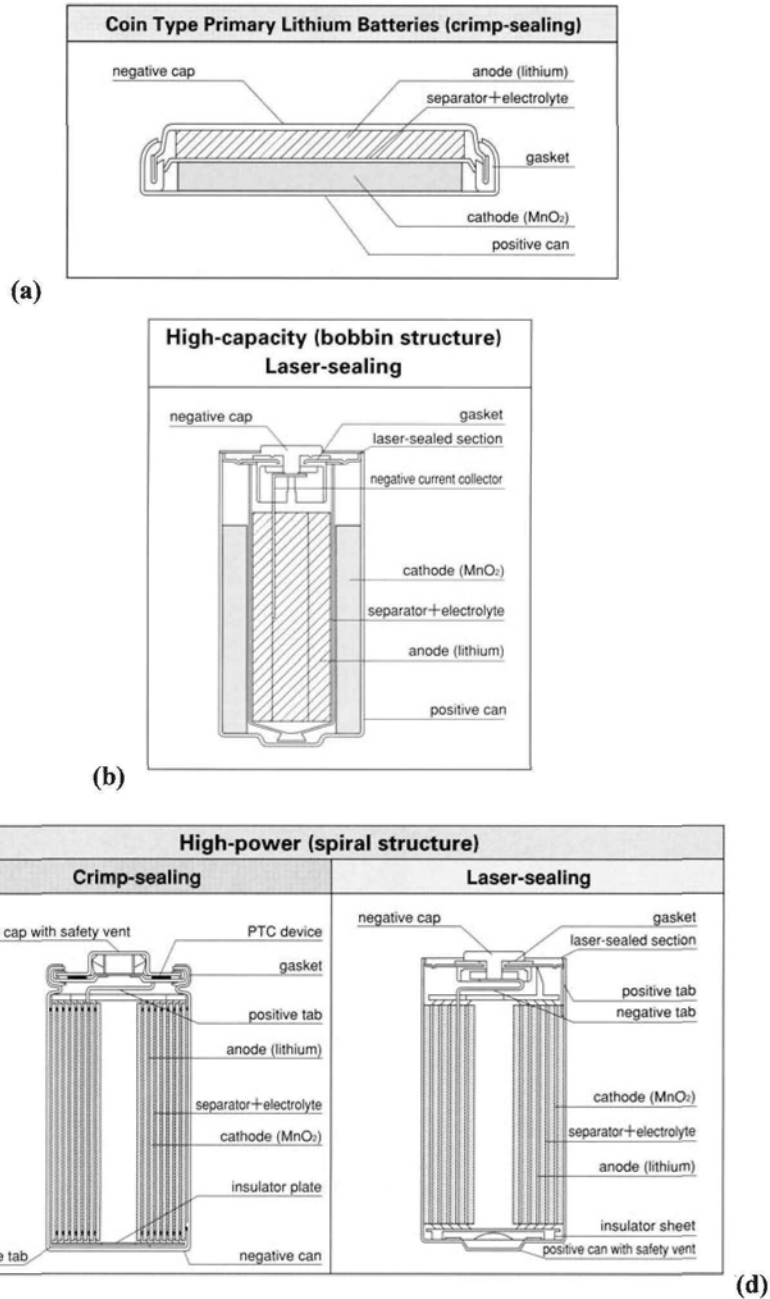
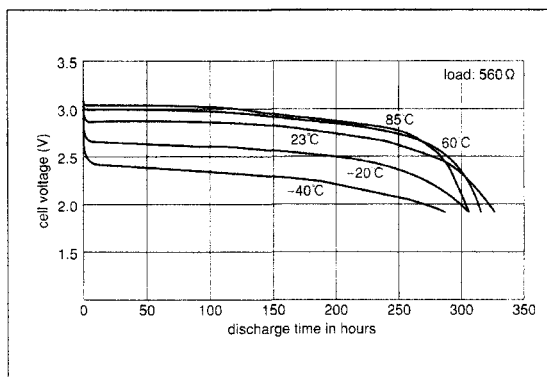
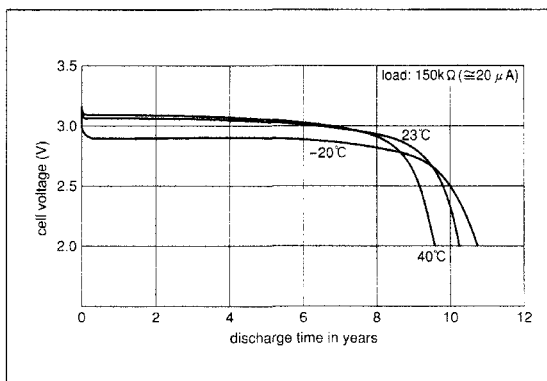


Figure 4.11. Cross-sections of coin (a), bobbin type cylindrical (b), spirally wound cylindrical with crimp sealing (c) and laser sealing (d) Li-MnO<sub>2</sub> cells. (Courtesy of Sanyo)

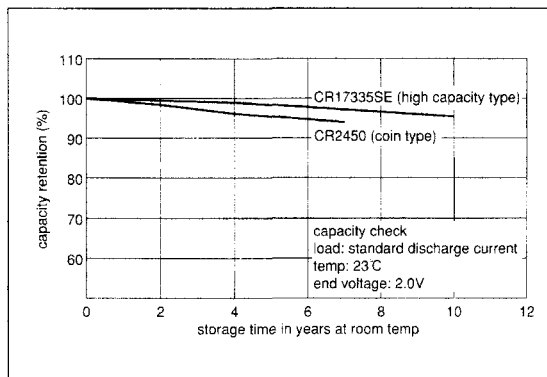




(a)



(b)



(c)

Figure 4.12. (a) Temperature characteristics of a spirally wound Li/MnO<sub>2</sub> cell (CR17335E-R, see Table 4.10, 1500 mAh,  $\sim 5$  mA); (b) low-rate discharge vs. temperature for a bobbin-type cell (CR17335SE, 1800 mAh); (c) storage characteristics for a button cell (CR2450) and a bobbin type cylindrical cell (CR17335SE). (Courtesy of Sanyo)

The Li/MnO<sub>2</sub> system is also available as a prismatic 9 V battery of the same shape as Zn-C or alkaline cells (see Figure 4.2). However, their internal construction is quite different. Each of the three cells in series contains stripes of anode, cathode and separator, just as in spirally wound cylindrical cells, bent so as to completely fill the space. These consumer- replaceable batteries last up to 5 times longer than alkaline and 10 times longer than Zn-C batteries [25].

Very thin “paper” cells, with thicknesses of 1-2 mm are also available [25]. Typical low-discharge rate applications include: smart security cards, bank theft tracking systems, electronic record tracking systems, *etc.*

In Table 4.11, typical applications for coin and cylindrical cells are reported. Cylindrical cells can reach capacities of 10-11 Ah in the approximate D size [25]. Such high capacity and high rate cells can find a number of heavy-duty applications in the safety, military, industrial and medical areas. An interesting new application is in a system that monitors sensors around a car and automatically sends an emergency message with car location in case of road accident [25].

#### 4.7.3. Li/CF<sub>x</sub> Batteries

Another interesting primary battery is the one using polycarbon fluoride, (CF<sub>x</sub>)<sub>n</sub>, as a cathode. This compound is synthesized by direct fluorination of carbon, in the form of graphite or coke, with fluorine gas at temperatures of 300°C to over 600°C. Covalent C-F bonds are formed in a structure resembling that of the initial carbonaceous material [26]. The value of *x* ranges from 0.9 to 1.2, and useful cathode material have *x* ≥ 1. In the following this cathode material will simply be written as CF<sub>x</sub> (where *x* is normally equal to 1).

This system was one of the first to be commercialized, especially for its high energy content, even at high temperatures, and flat voltage.

##### 4.7.3.1. Materials, Electrode Reactions, Cell Types and Performance

At the anode the reaction is:  $\text{Li} \rightarrow \text{Li}^+ + e$

At the cathode, assuming *x*=1:  $\text{CF} + e \rightarrow \text{C} + \text{F}^-$

Overall reaction:  $\text{Li} + \text{CF} \rightarrow \text{LiF} + \text{C}$

Table 4.10. Examples of primary Li/MnO<sub>2</sub> batteries. (Courtesy of Sanyo)**Coin Type Batteries** (Operational temperature range: -20°C to 70°C)

Model	Nominal voltage (V)	Nominal cap. (mAh)	Standard discharge current (mA)	Max. discharge current (mA)		Max. dimensions (mm)		Weight (g)
				continuous	pulse	diameter	height	
CR1220	3	36	0.1	2	10	12.5	2.0	0.8
CR2016	3	80	0.3	5	50	20.0	1.6	1.7
CR2025	3	150	0.3	5	40	20.0	2.5	2.5
CR2430	3	280	0.3	5	50	24.5	3.0	4.0
CR2450	3	610	0.2	2	30	24.5	5.0	6.9

**High-power Cylindrical Type Batteries (spiral structure, crimp sealing)** (Operational temperature range: -40°C to 60°C)

Model	Nominal voltage (V)	Nominal cap. (mAh)	Standard discharge current (mA)	Max. discharge current (mA)		Max. dimensions (mm)		Weight (g)
				Continuous	pulse	Diameter	height	
CR-1/3N	3	160	2	60	80	11.6	10.8	3.3
CR123A	3	1400	10	1500	3500	17.0	34.5	17
CR-V3	3	3300	20	3500	7000	29.0 (L)×14.5 (W)×52.0(H)		38
2CR5	6	1400	10	1500	3500	34(L)×17(W)×45 (H)		40

**High-power Cylindrical Type Batteries (spiral structure, laser sealing)** (Operational temperature range: -40°C to 85°C)

Model	Nominal voltage (V)	Nominal cap. (mAh)	Standard discharge current (mA)	Max. discharge current (mA)		Max. dimensions (mm)		Weight (g)
				continuous	pulse	diameter	height	
CR17335E-R	3	1500	5	700	2500	17.0	33.5	16
CR17335HE-R	3	1350	5	1000	3000	17.0	33.5	16
CR17450E-R	3	2200	5	1000	2500	17.0	45.0	22

**High-capacity Cylindrical Type Batteries (bobbin structure, laser sealing)** (Operational temperature range: -40°C to 85°C)

Model	Nominal voltage (V)	Nominal cap. (mAh)	Standard discharge current (mA)	Max. discharge current (mA)		Max. dimensions (mm)		Weight (g)
				continuous	pulse	diameter (D)	height (H)	
CR14250SE	3	850	0.5	7	70	14.5	25.0	9
CR17335SE	3	1800	1.0	8	100	17.0	33.5	17
CR17450SE	3	2500	1.0	9	150	17.0	45.0	22
CR23500SE	3	5000	1.0	10	200	23.0	50.0	42

Table 4.11. Applications of Li/MnO<sub>2</sub> cells as a function of cell sizes and characteristics. (From Ref. 3)

Application Parameters	Recommended Cell Type	Typical Applications
<ul style="list-style-type: none"> <li>• Small, low profile, lightweight battery with capacity of 75 to 550 mAh</li> <li>• Low drain (4 mA maximum on continuous drain and 20 mA maximum pulse)</li> <li>• Demanding storage or operating temperatures: -20°C to 60°C</li> <li>• Long shelf life of approximately 5 to 10 years with minimal loss in capacity</li> <li>• Worldwide availability at retail</li> </ul>	Coin Cell	<ul style="list-style-type: none"> <li>• Memory back-up</li> <li>• Watches</li> <li>• Calculators</li> <li>• Medical equipment</li> <li>• Electronic games</li> <li>• Security devices</li> <li>• Small, low power electronic devices</li> <li>• Automatic sensors and transmitters</li> </ul>
<ul style="list-style-type: none"> <li>• Cylindrical cell with capacity of 650 to 1900 mAh</li> <li>• Low drain (5 mA maximum on continuous drain and 20 mA maximum pulse)</li> <li>• Demanding storage or operating temperatures: -20°C to 60°C</li> <li>• Long shelf life of approximately 5 to 10 years with minimal loss in capacity</li> <li>• OEM replacement only</li> </ul>	Bobbin Cell	<ul style="list-style-type: none"> <li>• Memory back-up</li> <li>• Real time clock/calendar</li> <li>• Low power electronic devices</li> </ul>
<ul style="list-style-type: none"> <li>• Lightweight battery with capacity of 160 to 1300 mAh</li> <li>• Continuous drain of up to 1.2 A or intermittent drain with current pulses of up to 5 A</li> <li>• Immediate start-up capability at -20°C to 60°C</li> <li>• Minimal loss in performance and in rate capability after long periods of storage and/or intermittent usage</li> <li>• Long shelf life of approximately 5 to 10 years with minimal loss in capacity</li> <li>• Assurance of safety without compromising power</li> <li>• Worldwide availability at retail</li> </ul>	Spiral-Wound Cell	<ul style="list-style-type: none"> <li>• Small power tools</li> <li>• Alarms and detection devices</li> <li>• Communications equipment</li> <li>• High-performance flashlights</li> <li>• Medical instruments</li> <li>• Remote sensing devices</li> <li>• Handheld test apparatus</li> <li>• Utility meters</li> <li>• Flash cameras</li> <li>• Computers</li> <li>• Access controls</li> <li>• Laser devices</li> <li>• Bar code readers</li> <li>• Memory back-up</li> <li>• Real-time clock</li> </ul>

The formation of carbon enhances the electronic conductivity of the cathode. Typical electrolytes useful for this system are:  $\text{LiAsF}_6$  in BL or  $\text{LiBF}_4$  in PC-DME.

The  $\text{Li}/\text{CF}_x$  system has a number of pleasant features. Its operating voltage is flat and high ( $\sim 2.8$  V), its capacity is quite high at low-moderate drains, its useful temperature range is wide ( $-40^\circ\text{C}$  to  $+85^\circ\text{C}$ , and up to  $125^\circ\text{C}$  for some cells), and its self-discharge rate is the lowest of any primary Li cell.

This last feature is particularly notable: a  $\text{Li}/\text{CF}_x$  cell loses less than 0.5% capacity after one year of storage at room temperature, and less than 4%/year at  $70^\circ\text{C}$ . These tests were run for a period of 10 years, and the capacity loss tends to be lower at longer storage times. This is attributed to the inherent thermal and chemical stability of the C-F covalent bond in  $\text{CF}_x$ , and to the use of stable electrolytes [26].

Pin, coin, cylindrical and prismatic cells are available, with capacities ranging from 25 mAh to 5 Ah (Table 4.12). Service lives of different coin cells are shown in Figure 4.13. In Figure 4.14, the duration as a function of temperature is shown for a cylindrical cell. This system maintains a good proportion of its capacity at low temperatures, but at  $-40^\circ\text{C}$  a remarkable voltage drop has to be taken into account.

The applications of these cells depend on their design:

- Pin type: fishing pole tip lights, LED illumination, microphones.
- Coin type: calculators, cameras, low-power consuming cordless appliances, watches, memory backup.
- High temperature coin cells: automotive electronic systems, toll way transponders, RFID (radio frequency identification).
- Cylindrical type: utility meters, emergency signal lights, electric locks, electronic measurement equipment.

#### 4.7.4. $\text{Li}/\text{FeS}_2$ Batteries

These batteries have a nominal voltage of 1.5 V and, so, are interchangeable with aqueous batteries of the same voltage.

The electrode reactions are:



Table 4.12. Types of Li/CF<sub>x</sub> cells. All models of this category have the prefix BR. (Courtesy of Panasonic)

Model	Capacity (mAh)	Drain <sup>1</sup> (mA)	Dimensions (mm)		Weight (g)
Pin Type					
425	25	0.5	4.2	25.9	0.55
435	50	1.0	4.2	35.9	0.85
Coin Type					
1216	26	0.03 <sup>2</sup>	12.5	1.60	0.6
1220	35		12.5	2.00	0.7
1616	48		16.0	1.60	1.0
1632	120		16.0	3.20	1.5
2016	75		20.0	1.60	1.5
2020	100		20.0	2.00	2.0
2032	190		20.0	3.20	2.5
2320	110		23.0	2.00	2.5
2325	165		23.0	2.50	3.2
2330	255		23.0	3.00	3.2
3032	500		30.0	3.20	5.5
High Temperature Coin Type (-40 – 125°C) <sup>3</sup>					
1225A	48		12.5	2.5	0.8
1632A	120		16.0	3.2	1.5
2330A	255		23.0	3.0	3.2
2450A	550		24.5	5.0	5.0
2477A	1000		24.5	7.7	8.0
2777A	1000		27.5	7.7	8.0
Cylindrical Type					
C	5000	150.0	26.0	50.5	42.0
A	1800	2.5	17.0	45.5	18.0
AH	2000	2.5	17.0	45.5	18.0
AG	2200	2.5	17.0	45.5	18.0
2/3A	1200	2.5	17.0	33.5	13.5
2/3AH	1350	2.5	17.0	33.5	13.5
2/3AG	1450	2.5	17.0	33.5	13.5

1. Standard continuous drain; 2. Same value for all cells. 3. Same drain of the common coin type.

In fact, the reduction of FeS<sub>2</sub> (pyrite) in nonaqueous electrolytes (for this cell, LiI in a solvent blend) proceeds as a multi-stage process, in which FeS or Li<sub>2</sub>FeS<sub>2</sub> are formed prior to Fe [27]. Indeed, in light drain discharges, two voltage plateaus are visible at ~1.8 V and ~1.6 V.

Button type Li/FeS<sub>2</sub> batteries were used as a replacement of Zn/Ag<sub>2</sub>O batteries, but they are no longer produced and the only design available is the

spirally wound cylindrical one. An example of this battery is shown in Figure 4.15.

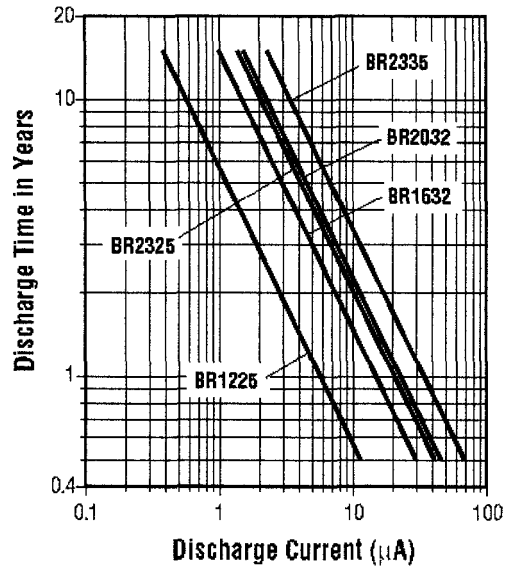


Figure 4.13. Service life vs. discharge current for several Li/CF<sub>x</sub> coin cells. (Courtesy of Rayovac)

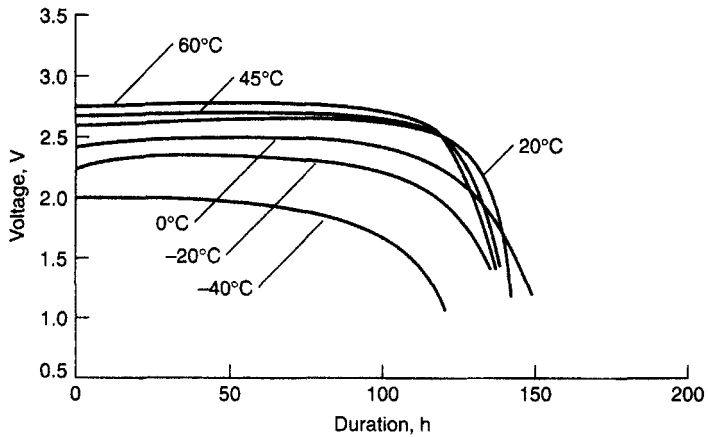


Figure 4.14. Discharge curves of a cylindrical 2/3A Li/CF<sub>x</sub> cell (1200 mAh) at various temperatures. Load: 300 ohms. (Courtesy of Panasonic)

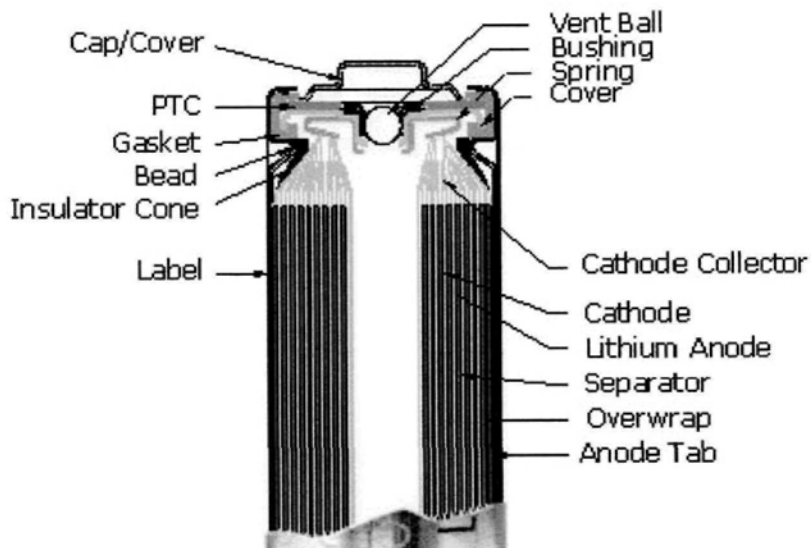


Figure 4.15. Section of an AA cylindrical Li/FeS<sub>2</sub> cell (only the upper part is shown). (From Ref. 28)

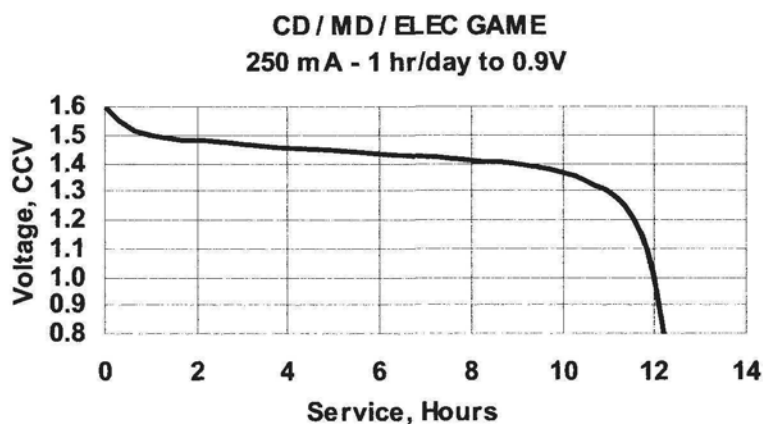


Figure 4.16. Voltage/service life curve of an AA Li/FeS<sub>2</sub> cell for applications requiring 250 mA (compact disk, minidisk, electronic game). (From Ref. 28)

This cell has a rated capacity of 2.5 Ah when a continuous current drain of 0.2 A is applied. This rather high capacity calls for a cell endowed with safety devices – in this case a vent ball to release excess internal pressure and a



positive temperature coefficient (PTC) device (see Chapter 7) for cutting excess current.

The operating voltage of the Li/FeS<sub>2</sub> cell is rather flat at low drains and moderately sloping at high drains. Figure 4.16 shows a voltage/service life curve in applications requiring 250 mA.

When compared with an analogous alkaline Zn/MnO<sub>2</sub> cell, the present system shows a higher and flatter voltage and, especially at high drains, longer service life. This means that the Li/FeS<sub>2</sub> cell has higher energy and power than the alkaline one. A comparison of the two cells in constant-power continuous discharges is shown in Figure 4.17. The Li cell lasts 2 to 4 times longer than the alkaline one.

Another pleasant feature of the Li/FeS<sub>2</sub> cell is its operating temperature range of -40 to 60°C. Its performance is obviously reduced below 0°C, but much less than that of the alkaline cell. Storage temperatures covering the above range are permitted. In particular, storing at ambient temperature for 10 years still allows recovering 90% of the original capacity [27].

#### 4.7.5. Li/SO<sub>2</sub> Batteries

This system provides an example of cathode material dissolved in the electrolyte and whose high reactivity with the Li anode is limited by the formation of a solid electrolyte interface. This battery and the one described in the next sub-section, Li/SOCl<sub>2</sub>, are characterized by high power, ability to work

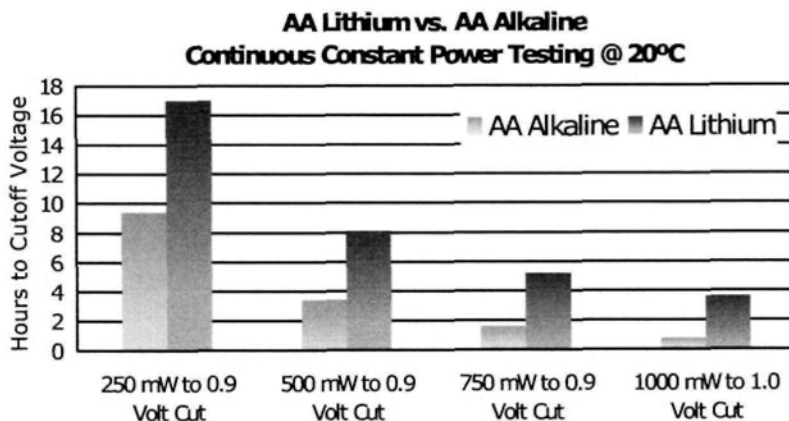


Figure 4.17. Comparison of the service lives of AA Li/FeS<sub>2</sub> and alkaline Zn/MnO<sub>2</sub> cells in various constant-power discharges. (From Ref. 28)

even at  $-60^{\circ}\text{C}$  and long shelf-life.

The Li/SO<sub>2</sub> battery is especially suitable for military/aerospace applications.

#### 4.7.5.1. Materials and Electrode Reactions

Li is the anode, while the cathode is porous carbon supporting the SO<sub>2</sub> reduction. The reactions are the following:



Li<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (Li dithionite) precipitates in the pores of the carbon cathode. Li<sub>2</sub>S<sub>2</sub>O<sub>4</sub> also forms on the Li anode as a protective film as soon as Li is exposed to SO<sub>2</sub>. The solvent, in this case, is acetonitrile (CH<sub>3</sub>CN) in which LiBr and SO<sub>2</sub> are dissolved. The high electrolyte conductivity, even at low temperatures, supports high drains in a wide temperature range.

#### 4.7.5.2. Cell Construction and performance

Li/SO<sub>2</sub> cells are available as spirally wound cylindrical cells. The presence of SO<sub>2</sub> requires a special construction: the electrolyte is kept in the liquid state by maintaining a pressure of 2 atmospheres within the cell. A safety vent is incorporated to cope with pressure values exceeding certain limits (*e.g.* 24 atmospheres). Acetylene black, used as a carbon, is mixed with Teflon as a binder and the mix is supported on an Al screen.

The capacity ranges from ~1 Ah for an AA cell to ~8 Ah for a D cell. However, cells of up to 25 Ah are also available. The larger cells can accept continuous currents of 2 A and pulse currents of 5 A. Their power capability is demonstrated by the fact that they can maintain a high proportion of their capacity even at the 1-hour discharge rate, whereas the capacity of Zn batteries start declining at the 20 to 50-hour rates.

The low-temperature performance is also noticeable, as shown in Figure 4.18: below  $0^{\circ}\text{C}$ , significant percentages of the rated capacity are recovered. At room temperature or above, the voltage remains flat at ~2.8 V.

These cells can be long stored even at temperatures as high as  $70^{\circ}\text{C}$ . This

is allowed by the hermetical cell construction and by the protective dithionate film formed on Li.

The main applications can be summarized as: sonobuoys, locator beacons, radio communications, and night vision.

#### 4.7.6. Li/SOCl<sub>2</sub> Batteries

Li/SOCl<sub>2</sub> cells have the highest energy density of all Li cells and their service life can reach 15-20 years. This last feature, coupled with the very low self-discharge, makes these cells ideal for applications where physical access is limited, *e.g.* in remote sensing systems.

##### 4.7.6.1. Materials and Electrode Reactions

Li is the anode, while the cathode is Teflon-bonded porous carbon supporting the reduction of SOCl<sub>2</sub>, and the electrolyte is LiAlCl<sub>4</sub> in SOCl<sub>2</sub> (the cathode material coincides with the solvent in this cell). Catalysts may be added to the carbon to favor the reduction reaction, while additives may be added to the electrolyte to improve the performance.

The electrode processes are:

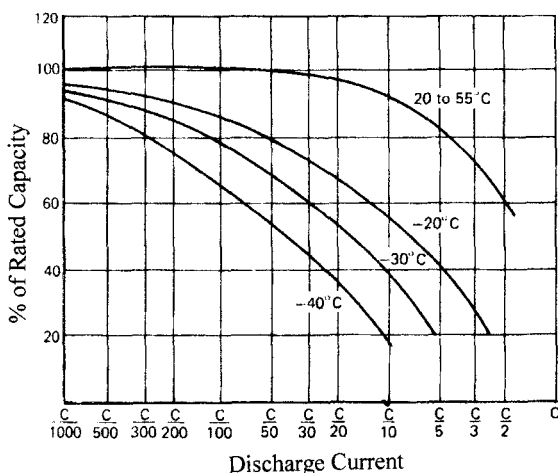
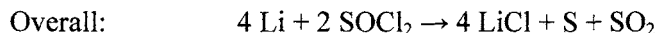
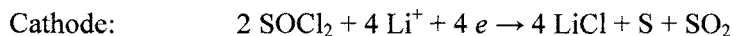


Figure 4.18. Capacity retention of a Li/SO<sub>2</sub> cell vs. current drain and temperature. (From Ref. 29)



S and SO<sub>2</sub> dissolve in the electrolyte, while LiCl precipitates into the carbon pores. Eventually, cathode clogging ends the cell operation.

A layer of LiCl is formed on the Li anode by the electrolyte, and this prevents further reaction and contributes to the outstanding shelf-life of this system. The low freezing point (-105°C) and relatively high boiling point (79°C) of thionyl chloride result in a battery capable of operating over a wide temperature range.

#### 4.7.6.2. Cell Construction and Performance

Li/SOCl<sub>2</sub> cells can be manufactured with different designs: bobbin type cylindrical, spirally wound cylindrical and disk type (in addition to large prismatic cells). All cell cases are hermetically sealed.

Bobbin type cells are highly suited for low-rate applications and long service lives. They manifest these features: temperature range, -55°C to 150°C; self-discharge, 1-2%/year at room temperature; high and flat voltage (>3 V); resistance to shock and to pressure variations; high capacity and energy. Cells discharged at currents in the μA range can deliver energy densities above 1000 Wh/L.

In Figure 4.19a, the voltage of an AA bobbin cells (2.4 Ah) is reported as a function of temperature for three rates. Voltages of 3.3-3.6 V are maintained at room temperature or above even at the highest rate (8C). Lower rates afford high voltages at temperatures well below 0°C.

The capacity of the same cell as a function of temperature is shown in Figure 4.19b. The rated capacity is delivered at 0.2 mA and room temperature, while 50% of this capacity can still be obtained at 20 mA and -20°C.

Typical applications of the high-capacity bobbin cells include: CMOS (complementary metal oxide semiconductor) memory backup, utilities and metering, telecommunications, medical devices, electronic toll tags, GPS (global positioning system) emergency locators, wireless security systems, animal tracking, *etc.* These cells can operate even at 150°C, a temperature encountered, *e.g.*, in oil prospecting.

Spirally wound cells are used in high power applications thanks to the high surface area of the cathode. This involves a couple of drawbacks: the energy output is reduced (more inactive material inside the cell) and the shelf-life is also shortened (the reactivity increases with surface area). Furthermore, the upper limit of the operating temperature range cannot overcome ~85°C.

These batteries are especially used in military applications, where high-drain and low-temperature operations are common. The C-size cells have capacities above 5 Ah and the D-size cells can reach 13 Ah. In continuous use, these cells can sustain currents of 800 and 1800 mA, respectively, with energy densities of 700-850 Wh/L.

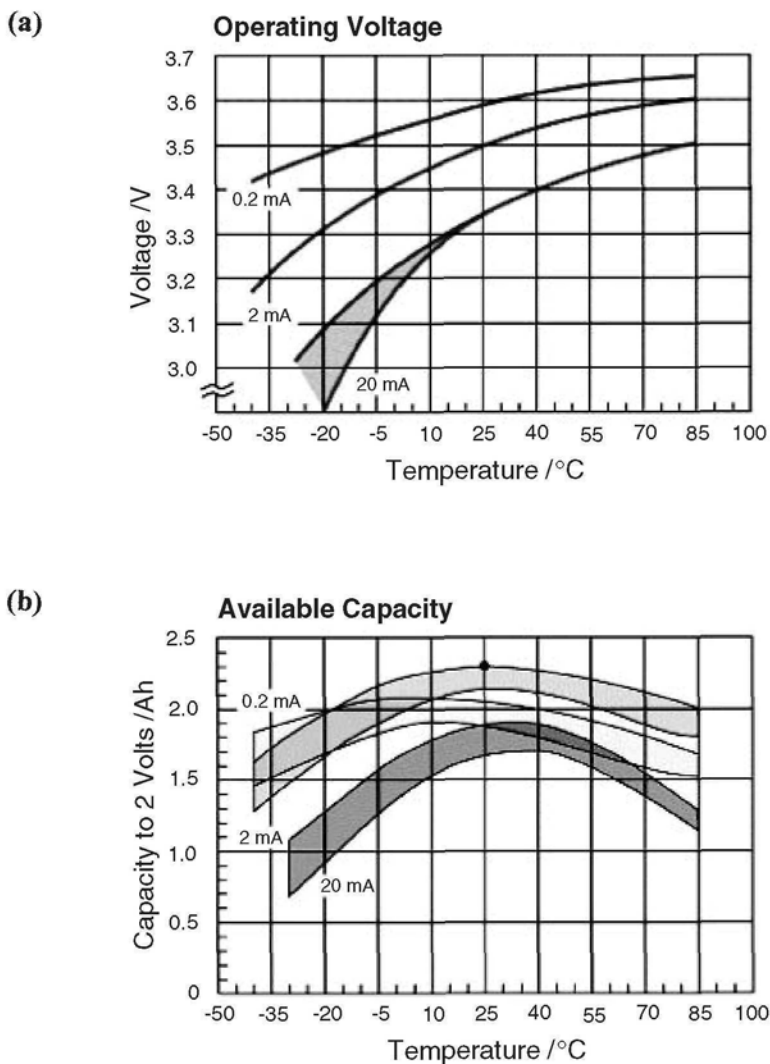


Figure 4.19. Operating voltage vs. temperature for an AA bobbin-type Li/SOCl<sub>2</sub> cell at three discharge currents (a); capacity vs. temperature for the same cell (b). (From Ref. 30)

Table 4.13. Comparison of the primary Li batteries of Sub-sections 4.7.2 – 4.7.6. (Adapted from Ref. 31)

Attribute/Cell	Li/SO <sub>2</sub>	Li/SOCl <sub>2</sub>	Li/MnO <sub>2</sub>	Li/CF <sub>x</sub>	Li/FeS <sub>2</sub>
<b>Voltage</b> (operating)	2.7	3.4	2.8	2.6	1.5
<b>S.E.</b> (Wh/kg)	280	550*	240	280	240
<b>E.D.</b> (Wh/L)	450	1000*	500	500	400
<b>P.D.</b> (pulse) (W/kg)	650	2500	80	250	
<b>Temp. Range</b> (°C)	-55 to 70	-40 to 150	-30 to 70	-30 to 70	-40 to 70
<b>Shelf-Life</b> (years)	10	10	10	15	10
<b>Market</b>	military	electronics military	electronics medical military	electronics medical	consumer
<b>Relative Market Size</b> (value)	5	15	100	1	1
<b>Relative Cost</b> (per kWh)	0.9	1.5	1	2	2

\* The original low values have been substituted by average values from other sources. (Note of the author)

## 4.8. Comparison of Primary Lithium Batteries

The Li batteries described in Sub-sections 4.7.2 to 4.7.6 are compared in Table 4.13 [31]. The energy and power values reported in this table are in reasonable agreement with those of other sources. However, the original values for Li/SOCl<sub>2</sub> appeared rather low and have been substituted with average values reported by others (see, for instance, Tables 1.1 and 2.3).

The Li/MnO<sub>2</sub> system is by far the most commercialized. Its main application is in digital cameras, as a replacement of two 1.5 V batteries. For instance the CR-V3 battery (see Table 4.10), formed by two cells in parallel, can replace 2 AA alkaline or Li/FeS<sub>2</sub> batteries. The other Li batteries occupy niches in the market. On the overall, the market has been steadily growing in the last 4-5 years at the rate of ~6%/year.

A comparison can be made between the Li batteries of Table 4.13 and the aqueous batteries reported in Table 4.9

## Chapter 5

# RECHARGEABLE BATTERIES

### 5.1. Introduction

In Chapter 2, a presentation has been made of the principal systems on which primary and secondary batteries are based. Some comparisons between the two classes have also been made (see Figures 2.1-2.4 and Table 2.3). Then, in Chapter 4, the most important primary batteries have been dealt with in detail. This chapter will highlight secondary batteries of interest for portable electric and electronic devices.

The development we are witnessing in this field would have been impossible without the introduction of rechargeable batteries progressively improved in terms of: size, energy, shelf-life, reliability, safety and cost.

Two of the systems used, Pb-acid and Ni-Cd, have a long history. The former dates back to 1859, while the latter was first manufactured in 1909. The others, rechargeable Zn/MnO<sub>2</sub>, Ni-MH, Li-ion (with liquid or polymeric electrolytes) are relatively young, but the contribution of the latter two systems has been of paramount importance for a truly portable electronic world.

The five main systems are compared in Table 5.1. Each will be more extensively analyzed in its section. However, Ni-Cd, Ni-MH and Li-ion will receive a greater attention because of their practical impact.

The values reported in Table 5.1, as well as the others reported in this book, are reasonably updated values for commercially available batteries. However, due the rapid advances of the Ni-MH and Li-ion systems, the need of a short-term update for these systems (especially the latter) has to be taken into account.

As is obvious, none of the batteries possesses to the same degree all the characteristics that are desirable in a battery. An attempt to rank the batteries based on some distinctive features is done in Table 5.2, in which values from different sources have been averaged.

As in the case of primary batteries, the initial choice for a given application is up to the manufacturer, but the user can make its own choice on the basis of the such consideration as: availability of alternatives, continuous or infrequent use, high or low temperature, recharge facilities, cost, *etc.*



## 5.2. Sealed Lead-Acid Batteries

Small Pb-acid batteries are available to power portable devices. These batteries can have capacities of 1.2 Ah only and weigh less than 300 grams. However, due to a rather low energy density, they cannot be used in common applications, as computers and cellular phones, but in special applications that will be later detailed.

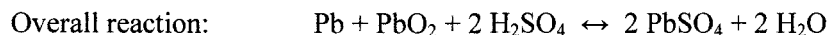
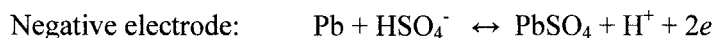
There is some confusion in the literature about the terms SLA (sealed lead-acid) and VRLA (valve regulated lead-acid). Both terms refer to Pb-acid batteries with a limited amount of immobilized electrolyte. Strictly speaking, the SLA is totally sealed, while the VRLA has a valve allowing to release excess internal pressure. The SLA is often referred to as “portable” and indicated as a low-capacity battery, while the VRLA is mentioned as a stationary battery, *e.g.* for uninterruptible power sources, of greater capacity.

In fact, the two terms tend to describe a battery with essentially the same construction, and are interchanged by manufacturers or, as done by Panasonic, VRLA batteries are introduced as “previously referred to as SLA”.

In this section, both terms are used and, in particular, the term VRLA includes low- to medium-capacity batteries for portable applications.

### 5.2.1. Cell Materials and Electrode Reactions

The chemistry of a VRLA battery is the same as the common Pb-acid battery with excess electrolyte. The negative electrode is Pb, the positive is PbO<sub>2</sub> and the electrolyte is a concentrated H<sub>2</sub>SO<sub>4</sub> aqueous solution. The reversible reactions\* are:



The main difference with the common, electrolyte-flooded Pb-acid battery is immobilization of the electrolyte and O<sub>2</sub> recycle permitted by this feature. The aqueous H<sub>2</sub>SO<sub>4</sub> solution can either be soaked into an absorbent glass mat (AGM) or gelled by addition of fumed SiO<sub>2</sub>. In both cases, the electrolyte

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\* In all secondary batteries reported in this book, the discharge process proceeds from left to right and the charge process from right to left.

cannot move, this resulting in some distinct advantages: a) the battery can be operated in any position; b) acid stratification is hindered or eliminated; c) there is enough free space inside the cell to allow for O<sub>2</sub> diffusion in the gaseous phase, which is more than 10<sup>5</sup> times faster than in the dissolved state [33].

The last piece of evidence determines the main characteristics of VRLA batteries, *i.e.* the internal O<sub>2</sub> cycle. An important secondary reaction of the Pb/PbO<sub>2</sub> system is the one occurring at the positive electrode:

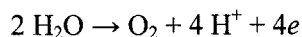
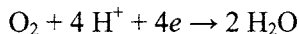


Table 5.1. Characteristics of rechargeable cells of commercial interest for portable devices. (Adapted From Ref. 32)

Characteristics/Cell	Ni-Cd	Ni-MH	Lead-Acid	Li-ion	Reusable Alkaline
<b>Specific Energy</b> (Wh/kg)	40-60	60-90	30-50	150-190	80 (initial)
<b>Energy Density</b> (Wh/L)	150-190	300-340	80-90	350-470	180 (initial)
<b>Cycle Life</b> (to 80% of initial capacity)	1000 to 1500	500 to 1000	200 to 300	500 to 1000	50 (to 50%)
<b>Fast Charge Time</b>	1h	1h	8-16h	2-3h	2-3h
<b>Overcharge Tolerance</b>	moderate	low	high	very low <sup>1</sup>	moderate
<b>Self-discharge / Month</b> (room temperature)	20%	30%	5%	<5%	0.3%
<b>Nominal Cell Voltage (V)</b>	1.25	1.25	2	3.7	1.5
<b>Load Current</b>					
- peak	20C	5C	10C	>2C	0.5C
- continuous	1C	0.5C or lower	1C	1C or lower	0.2C or lower
<b>Operating Temperature</b> (°C)(discharge only)	-40 to 60	-20 to 60	-20 to 60	-20 to 60 <sup>1</sup>	0 to 65
<b>Cost</b> (US\$/Wh)	0.25	0.5	0.5	0.8	
<b>Commercial Use Since</b>	1950	1990	1970	1991 <sup>2</sup>	1992

1. Improved in Li-ion polymer with Mn spinel as the positive electrode; 2. 1999 for polymeric.

In a VRLA cell,  $O_2$  can fast diffuse, in the gaseous phase, in the pores of the AGM not filled with electrolyte or in cracks of the gelled electrolyte. Therefore, it can reach the negative electrode and reform  $H_2O$ :



This reaction is fast and allows recovering of  $O_2$  generated at the positive, thus maintaining practically unchanged the  $H_2O$  amount in the electrolyte.

In the common Pb-acid battery,  $H_2$  and  $O_2$  are formed during charge and leave the cell, causing  $H_2O$  loss. In the VRLA battery, in addition to  $O_2$  recovery, there is little  $H_2$  evolution, which escapes the cell through the vent or through the plastic container itself. However, if the cell is overcharged at high rates ( $>C/3$ ), the internal pressure caused by excess  $H_2$  and  $O_2$  is released through the valve and the recombination process is partial. Therefore, overcharging at these rates has to be avoided.

### **5.2.2. Cell Construction and Performance**

VRLA can be made in cylindrical or prismatic configurations. For the latter, a thin version also exists. Only essential data on the electrode construction are mentioned here. More details on common and VRLA batteries can be found elsewhere [34].

The cylindrical design is based on thin grids of pure Pb containing 0.6% Sn for deep discharge recovery. The grids are thin to provide high surface area and high rates. They are pasted with  $PbO_2$  (subsequently treated to have the positive and negative electrodes) and spirally wound with the interposition of an AGM separator. The roll is stuffed into a polypropylene liner, and a top with a vent hole is added and bonded to the liner. The solution is then added and the relief valve is placed over the vent hole. The cell is then enclosed into a metal can and a crimped plastic cap completes the assembly. The metal container does not hinder operation of the valve. Monobloc batteries with two to six cylindrical cells are commercialized.

The VRLA prismatic cells have flat grids containing Ca-Pb alloys (without Sb) for reducing corrosion and gassing. This composition, however, makes the electrodes more sensitive to deep discharge [35]. At 30% depth of discharge (DOD), 1200 cycles may be obtained, but only 200 cycles at 100% DOD. Some additives, as  $H_3PO_4$ , help in this respect. The electrolyte is either absorbed on a glass-fiber separator or on fumed silica.

Table 5.2. Ranking of portable secondary batteries based on selected parameters. Best mark: 10; worst mark: 1.

Battery	Energy <sup>1</sup>	Power <sup>2</sup>	Low-Temp. Operation	Discharge <sup>3</sup> Profile	Shelf- Life	Efficiency <sup>4</sup>	Total Life	Cost <sup>5</sup>	Toxicity
Ni-Cd	4	10	10	8	4	6	10	8	1
Ni-MH	6	8	8	8	3	6	7	6	7
Pb-acid	4	6	8	6	8	8	8	8	1
Li-ion	10	7	8 <sup>6</sup>	7	8	10	9	7	7
Zn/MnO <sub>2</sub>	8	8	6	2	10	4	1	9	10

1. Average of specific energy (Wh/kg) and energy density (Wh/L); 2. Average of specific power (W/kg) and power density (W/L); 3. From flat to sloping; 4. Discharge/charge; 5. On a total Wh basis; 6. For Li-ion polymer.

SLA cylindrical batteries can stand high currents also at low temperatures. At room temperature, a cell providing full capacity at the 20-h rate can still give 60% of this capacity at the 1-h rate (Figure 5.1a). At  $-40^{\circ}\text{C}$  and 20-h rate, 50% of the rated capacity can still be recovered.

Self-discharge characteristics vs. temperature are presented in Figure 5.1b. The capacity retention is fair at room temperature or below and superior to that of Ni-Cd or Ni-MH batteries (see also Table 5.1). The state of charge of Pb-acid batteries when kept on storage is of the utmost importance. If long stored in the discharged state, sulphation of the electrodes occurs.  $\text{PbSO}_4$  formed during discharge adheres to the electrodes as a thin layer of very small particles. Long stand in the discharged state causes formation of large  $\text{PbSO}_4$  grains that can hardly be reconverted into active materials. Manufacturers recommend recharging the battery when the open circuit voltage falls to 2.05-2.07 V, which corresponds to 60-70% of the total capacity.

Charging of portable VRLA batteries can be fast (less than 4 h, some applications require 1 h) or relatively fast (5-7 h). The preferred technique is the constant current (CC), constant voltage (CV) charging (Figure 5.2). There is an initial charge at the 0.4C or higher rate (step I). In this step, the cell voltage increases gradually as the acid concentration increases (see overall reaction on page 78). When the cell voltage reaches  $\sim 2.45$  V, the charger switches into CV mode (step II) and monitors the decreasing current values. The charge is terminated at a preset (low) current.

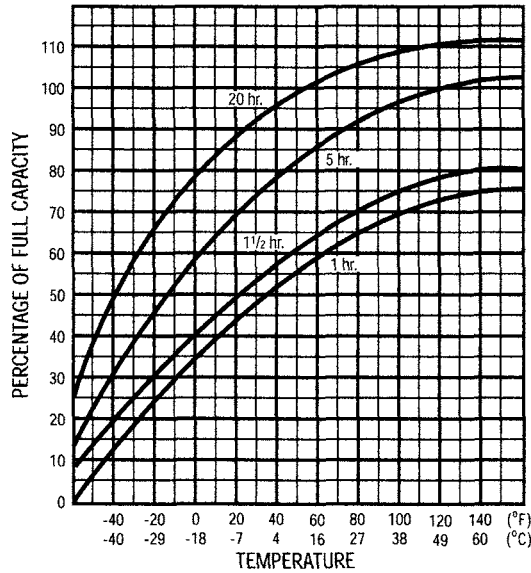
At this point, two ways of further prolonging the charge are possible. For a single cell to be left on stand, a float charge at a potential of  $\sim 2.25$  V may be applied to counterbalance self-discharge. The other additional charge is applied to VRLA multi-cell batteries (step III in Figure 5.2) and is called “equalizing”. Such extra-charge compensates for variations of the  $\text{O}_2$  cycle in individual cells. Cells with a higher rate for the  $\text{O}_2$  cycle (which acts as a parasitic current) may not reach full charge, and then can undergo a deeper following discharge. In the next charge, the situation will get worse (less charge accepted) and the state of charge of the cells becomes uneven. To eliminate this failure mode, cell equalizing is obtained with a short period of CV applied. Alternatively, equalizing may be obtained with a constant or pulsed current [33].

Examples of VRLA batteries are listed in Table 5.3. The main applications in portable devices can be summarized as:

- Portable TVs
- Tape recorders, radios
- Photographic equipment
- Measuring instruments
- Lighting equipment
- Various power toys and recreational equipment

(a)

**Capacity as Affected by Temperature**  
@ VARIOUS RATES OF DISCHARGE



(b)

**Typical Self-Discharge Characteristics**

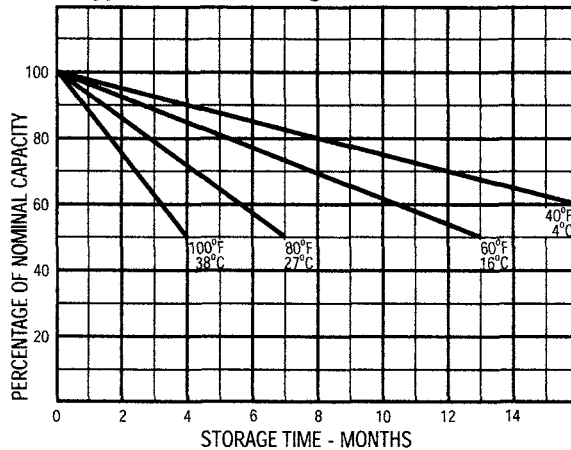


Figure 5.1. (a) Capacities of VRLA cylindrical batteries vs. temperature and rate; (b) self-discharge characteristics vs. temperature. (Courtesy of EaglePicher)

### 5.3. Sealed Nickel-Cadmium Batteries

The manufacture of sealed Ni-Cd batteries began in Europe in the 1950s and this was the battery used in portable devices up to 1990. Since then, Ni-MH

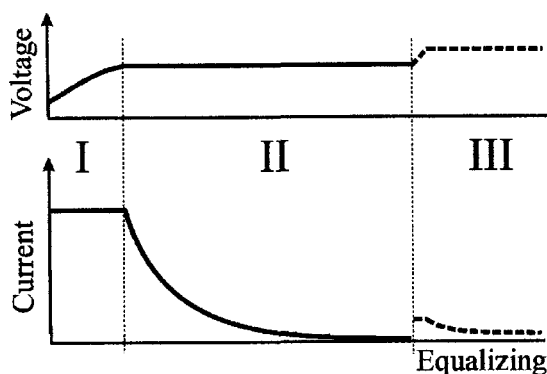


Figure 5.2. CC-CV charge of a VRLA battery with the equalizing step. (From Ref. 33)

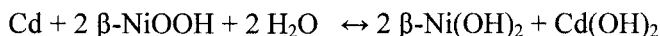
Table 5.3. Portable VRLA batteries (6 V). (Courtesy of Yuasa)

TYPE	Rated	Approx. Dimensions						Approx Weight	
	Capacity	Length		Width		Overall Height			
	(20 hr rate)					(with terminals)			
	(Ah)	mm	in	mm	in	mm	in	kg	lbs
NP1.2-6	1.2	97	3.82	25	0.98	54.5	2.15	0.29	0.64
NP3-6	3.0	134	5.28	34	1.34	64.0	2.52	0.63	1.93
NP4-6	4.0	70	2.76	47	1.85	105.5	4.15	0.85	1.87
NP7-6	7.0	151	5.94	34	1.34	97.5	3.84	1.26	2.78
NP8-6	8.0	151	5.94	50	1.97	97.5	3.84	1.70	3.75
NP10-6	10.0	151	5.94	50	1.97	97.5	3.84	1.90	4.19

and Li-ion batteries have gained increasing market shares especially in the most developed countries. However, the worldwide production of small Ni-Cd batteries is not decreasing, thanks to the contribution of countries where its favourable features (price among others) are still appreciated.

### 5.3.1. Cell Materials and Electrode Reactions

A charged Ni-Cd battery has Cd as a negative and  $\beta$ -NiOOH (nickel oxyhydroxide) as a positive electrode. In an alkaline solution (KOH plus some LiOH), these materials give rise to the overall, reversible reaction:



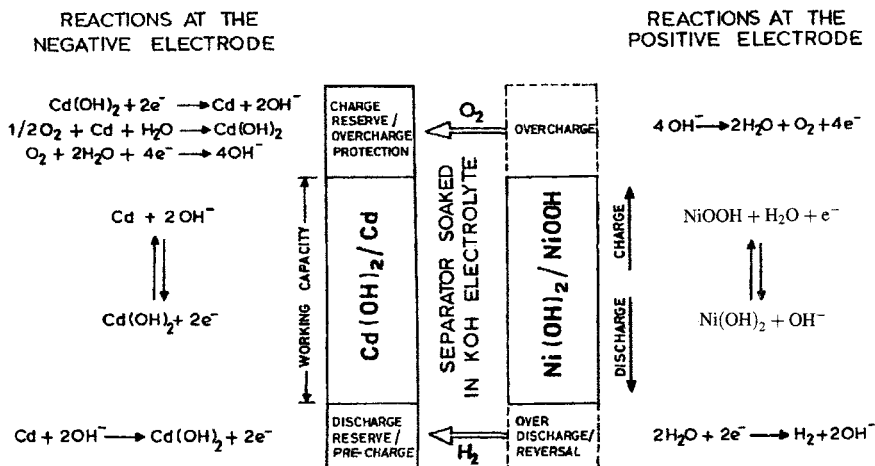
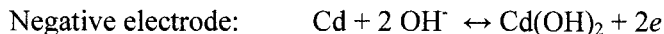


Figure 5.3. Scheme of all reactions occurring in a sealed Ni-Cd cell. (From Ref. 36)

However, several reactions occur at the electrodes, as shown by the scheme of Figure 5.3. The reactions determining the battery capacity are:



It is noteworthy that the reversible reduction of NiOOH to Ni(OH)<sub>2</sub> involves the intercalation of a hydrogen ion into the layered structure of the former, this giving rise to a solid solution. This is a process favoring the long-term reversibility of an electrode.

In sealed Ni-Cd cells too there is recombination of the oxygen generated at the positive electrode during overcharge. Indeed, the cell is constructed so to be positive-limited and, on overcharge, O<sub>2</sub> is formed and diffuses through the separator to the negative electrode where is reduced to OH<sup>-</sup> (see Figures 5.3 and 5.4). The Cd(OH)<sub>2</sub> formed is converted into metallic Cd during cell charge.

The negative to positive capacity ratio is normally between 1.5 and 2. The overcharge protection is ~30% of positive capacity, while the discharge reserve is 15-20% (see again Figure 5.3) [36]. Repeated overdischarges of cells in series in a battery (due to cells imbalance) generate OH<sup>-</sup> and H<sub>2</sub>. The former recombines with Cd, while the latter is only slowly consumed, so that it can



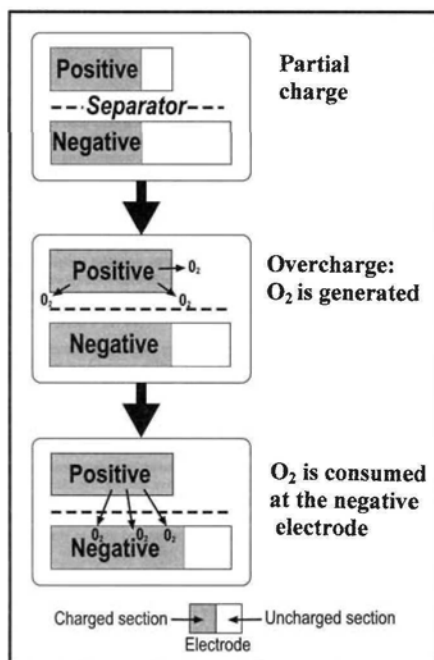


Figure 5.4. Mechanism of recombination of  $O_2$  generated at the positive electrode of the sealed Ni-Cd battery on overcharge. (From Ref. 37)

accumulate in the cell and may escape through the safety valve in case of overpressure (see later) [36].

The construction of the positive electrode is of the utmost importance in determining its performance. Here, the most common techniques will be summarized.

An important milestone in the development of nickel electrodes is the sintered-plate technology. A porous sintered substrate is first created, which is then impregnated with the active material. The sintered substrate (or plaque) is prepared with a wet-slurry process: on both sides of a nickel or nickel-plated grid, a viscous slurry based on carbonyl nickel is applied. After drying to eliminate  $H_2O$ , the plaque is sintered at  $800-1000^\circ C$  in a reducing atmosphere. The loose Ni particles adhere strongly to one another forming a high surface-area substrate with innumerable fine pores having a diameter of several microns. These pores are filled with aqueous  $Ni(NO_3)_2$  which is converted chemically or electrochemically into  $Ni(OH)_2$  [36]. The porous plaque is characterized by good mechanical strength and high conductivity. The electrodes so formed have

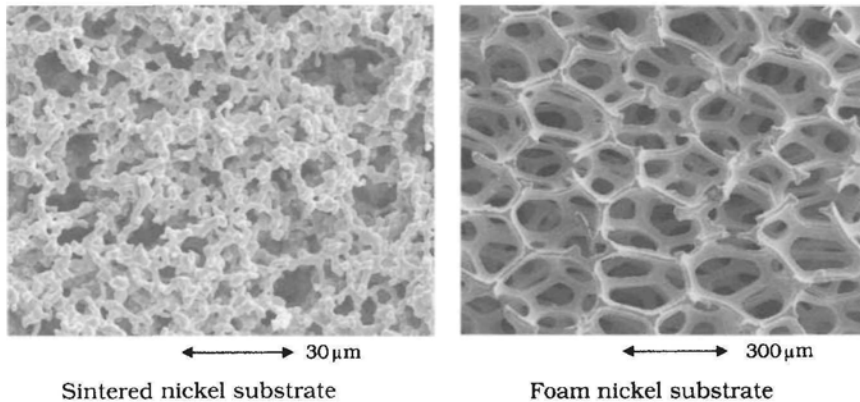


Figure 5.5. Sintered and foam nickel substrates for sealed Ni-Cd batteries. (From Ref. 38)

a relatively high inert to active material weight ratio, this limiting their capacity, and are suitable for high drain applications and fast charges.

Another construction uses high-porosity nickel foam as a substrate loaded with spherical  $\text{Ni}(\text{OH})_2$  particles. These pasted electrodes have lower cost and higher energy density with respect to sintered electrodes. This latter feature is due to the higher pore volume of the substrate in which more active material can be accommodated. Figure 5.5 shows micrographs of sintered and foam Ni substrates [38].

Finally, the positive electrode can have a fibrous structure, obtained by Ni-plating a mat of synthetic fibres (graphite or plastic) followed by sintering at  $800^\circ\text{C}$  to form substrates with 90% free volume, which are impregnated with the active material.

The negative electrode can be, in turn, of the sintered or non-sintered type. In the first case, the micropores of the substrate are filled with  $\text{Cd}(\text{OH})_2$  (derived from a nitrate solution). The non-sintered type is obtained by coating a Ni-plated steel grid with a CdO-based paste.

### 5.3.2. Cell Construction and Performance

Ni-Cd batteries are produced with cylindrical, prismatic or button shapes, the first two being more commercialized.

A cylindrical battery normally uses a thin sintered-plate positive electrode wound with a thin sheet of separator (polyamide or polypropylene) and negative electrode. The roll is stuffed into a metal casing and the alkaline solution is

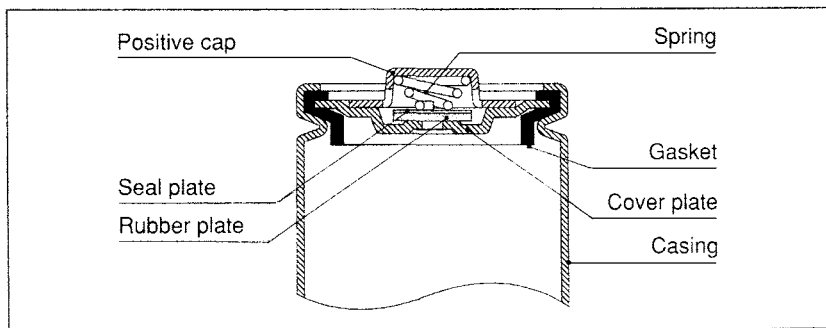


Figure 5.6. Upper part of a cylindrical Ni-Cd cell with the resettable gas release vent. (From Ref. 39)

added. The battery is then sealed with a plate endowed with a resetting vent, to release excess gas. The upper part of a cylindrical cell is shown in Figure 5.6. The spring under the cap allows rising of the plate, in case of overpressure, to release gas. When the pressure drops to a normal level, the vent resets permitting normal operation. However, repeated venting reduces capacity and cycle life [39].

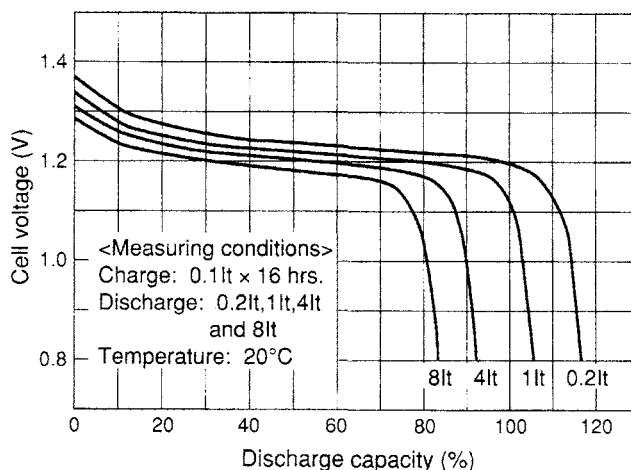


Figure 5.7. Discharge curves at various rates of standard Ni-Cd batteries. "It" corresponds to C. (Courtesy of Sanyo)

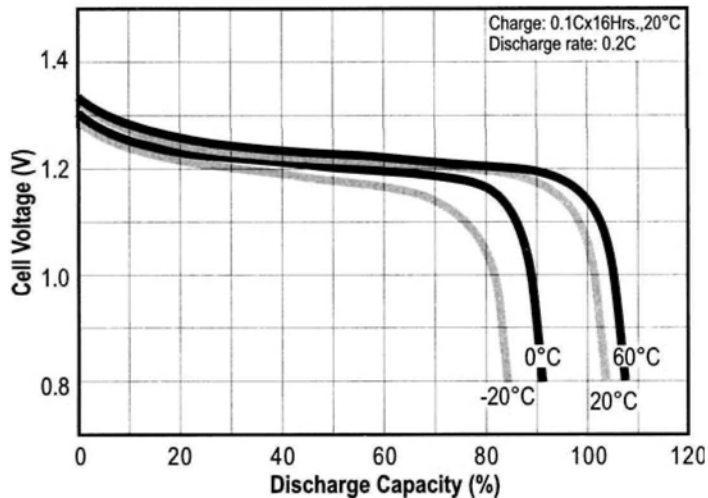


Figure 5.8. Effect of temperature on the capacity of Ni-Cd batteries discharged at the standard 5-hour rate (0.2C). (From Ref. 37)

Prismatic Ni-Cd batteries are normally produced in slim configuration. In multi-cell batteries, this shape permits better space exploitation in comparison with the cylindrical shape, so their volumetric energy density is higher. The electrodes are manufactured as previously described and cut into flat plates. These cells too are endowed with a resettable gas vent. Larger prismatic cells contain fibre-structured electrodes providing high surface area and, therefore, high rate capability.

In general, even the standard grade Ni-Cd batteries can sustain high currents, as shown in Figure 5.7. A 16-time increase in the discharge rate still allows recovering 85% of the rated capacity.

Another nice feature of these batteries is their low temperature behavior. At the standard 5-hour rate, a large fraction of the rated capacity can be recovered, as shown in Figure 5.8. This is due to the fact that the internal resistance remains low even below 0°C. The performance is also good at high temperatures: typical operation range is -20°C to 60°C. Furthermore, both the lower and upper limit can be increased in special configurations.

Most Ni-Cd batteries can be stored in the temperature range -30/-40°C to 50/60°C without significant performance deterioration. Some batteries have been stored for up to 10 years and could still deliver, after recharge, almost 100% of their original capacity [37]. However, the ability to maintain the charge is not outstanding in comparison with other systems (see also Table 5.1). As shown in Figure 5.9, both sintered and pasted electrodes lose rapidly their charge even at room temperature.

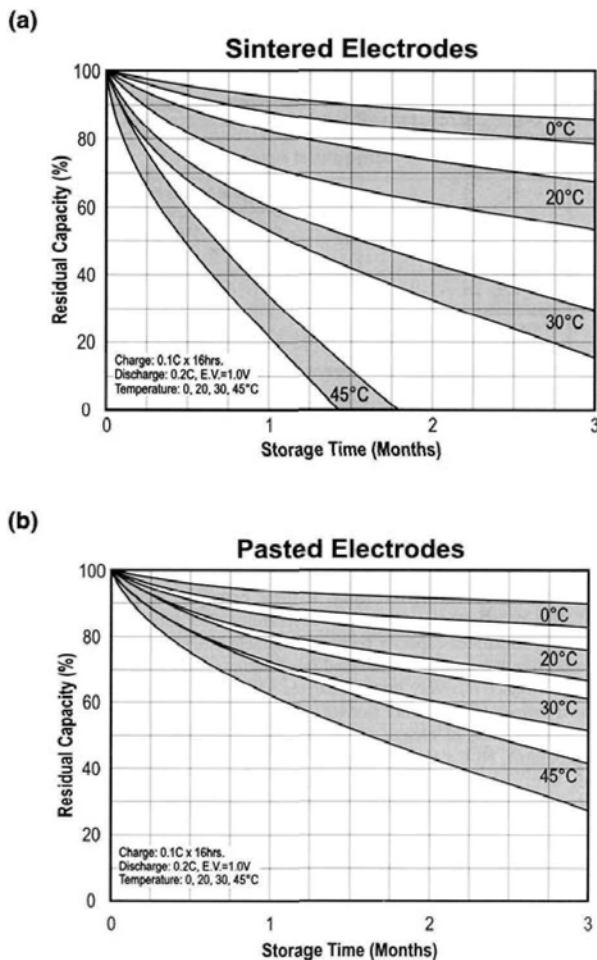


Figure 5.9. Self-discharge characteristics of cylindrical Ni-Cd batteries with sintered (a) and pasted (b) electrodes. (From Ref. 37)

The faster self-discharge of batteries with sintered electrodes is connected with their higher surface area (see previous sub-section). Indeed, this favors chemical reactions that mimic the electrochemical ones and rapidly bring the battery to a discharged state, especially above temperatures of  $\sim 30^{\circ}\text{C}$ .

Charging of the Ni-Cd battery is done at constant current. For commercial cells, rates of 0.1–0.2C are usually applied. However, some cells can be charged at the C (1-hour) rate, with charge control. Figure 5.10 depicts charging curves at two rates. The maximum in the voltage, which is typical of this system and of the Ni-MH system, signals the end of the  $\text{Ni}^{\text{II}} \rightarrow \text{Ni}^{\text{III}}$  oxidation at the positive

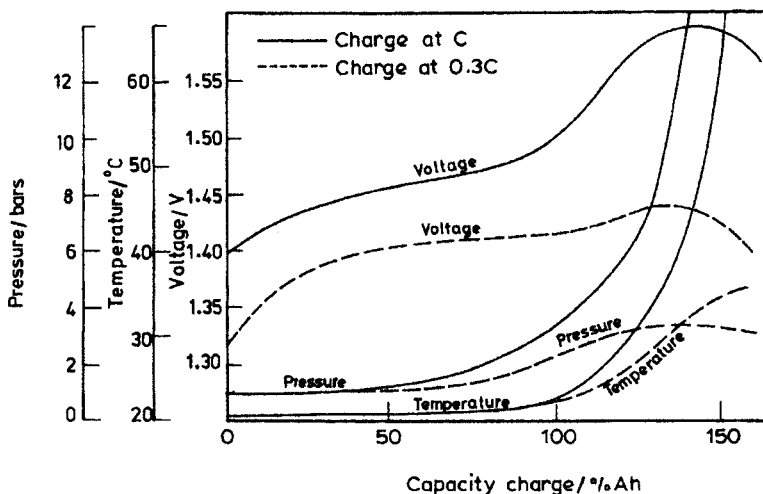


Figure 5.10. Shapes of the charging curves of standard Ni-Cd batteries at different rates. (From Ref. 36)

electrode. As explained in more detail in Chapter 7, peak voltage detection is one of the criteria used for stopping the charge. However, as shown in Figure 5.10, peak detection becomes less defined as the charging rate decreases. The same is true if the temperature approaches or exceeds 40°C. In these cases, other criteria may be applied, such the rate of temperature increase ( $\Delta T/\Delta t$ , see again Chapter 7). To reach full charge, an input providing more than the theoretical capacity has to be given (e.g. 140%). Furthermore, self-discharge can be tackled by leaving the cell on float or trickle charge, that is a charge with a rather low current. Thanks to the  $O_2$  recombination process, long standing on trickle charge is not detrimental for the battery performance.

Fast charge is possible in batteries with electrode structures and electrolyte distribution able to enhance  $O_2$  recombination. Therefore, in these batteries, the internal pressure remains low throughout the charging process, whereas in standard batteries a steep increase is observed – see Figure 5.10.

The basic features of the discharge and charge processes and those of storage have been so far described. In particular, their sensitivity to the temperature has been stressed. In Table 5.4, the effects of low and high temperatures on storage, discharge and charge are summarized. It is noteworthy that discharging can be made in a relatively wide range (see also Figure 5.8), but charging, especially if fast, must be done in a narrower range. Charging below the recommended temperature may cause  $O_2$  overpressure and consequent

Table 5.4. Effects of high and low temperature on storage, discharge and charge of Ni-Cd batteries. (From Ref. 39)

	Low Temperature	High Temperature
<b>Storage</b> (All Types)	<b>- 40°C</b> No detrimental effect. However, cells or batteries should be allowed to return to room temperature prior to charging.	<b>60°C</b> No detrimental effect. However, self-discharge is more rapid starting at 32°C and increases as temperature is further elevated.
<b>Discharge</b> (All Types)	<b>- 20°C</b> No detrimental effect but capacity will be reduced.	<b>45°C</b> No detrimental effect.
<b>Charge</b>		
(7-10 hour rate)	<b>0°C</b> Cells or batteries should not be charged below 0°C at the 7 - 10 hour rate.	<b>45°C</b> Cells or batteries evidence charge acceptance of approximately 50%.
(1-3 hour rate)	<b>15°C</b> Cells or batteries should not be charged below 15°C at the 1 hour rate or below 10°C at the 3 hour rate.	<b>45°C</b> Cells or batteries evidence charge acceptance of approximately 90%.

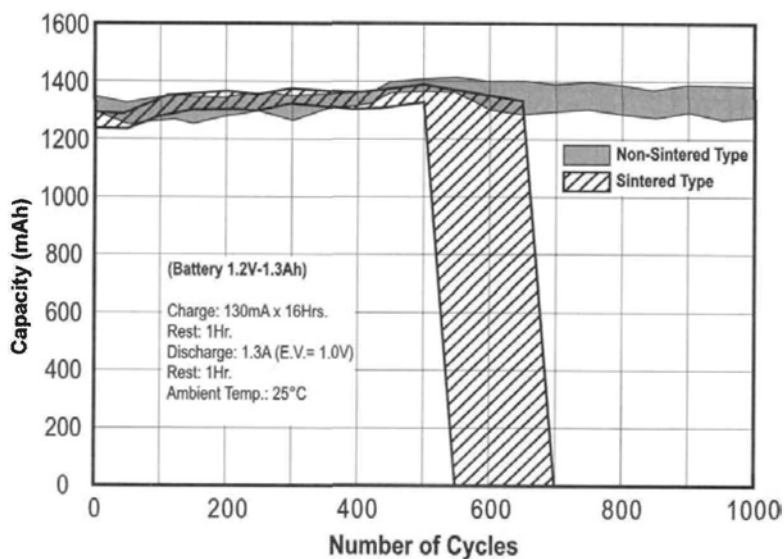


Figure 5.11. Cycling of Ni-Cd batteries with sintered and non-sintered electrodes. (From Ref. 37)

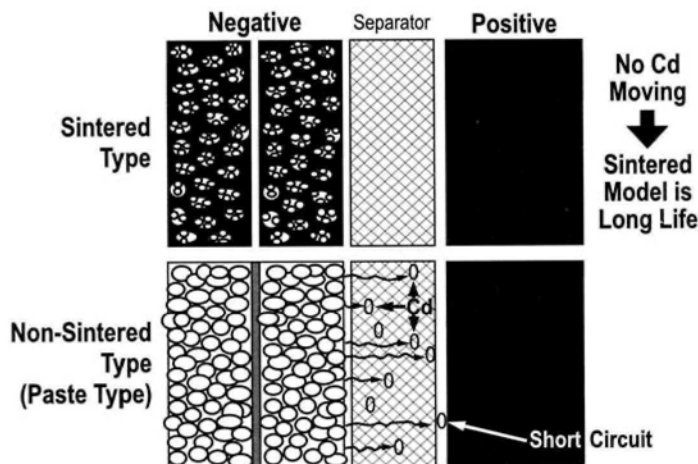


Figure 5.12. Cd migration in a non-sintered (pasted) electrode. (From Ref. 37)

opening of the safety vent. As previously mentioned, repeated openings shorten the cycle life.

In comparison with VRLA batteries, Ni-Cd batteries experience minor degradation at high temperatures and perform much better at low temperatures (see Figures 5.1 and 5.8).

The Ni-Cd system enjoys long cycle life provided that some conditions are applied (temperature, rate, depth of discharge, correct charging, *etc.*).

Sintered electrodes provide longer cycle lives than non-sintered ones, as shown in Figure 5.11. This is connected with the migration of metallic Cd particles, less strongly bound to their substrate, from the negative to the positive electrode, thus causing short circuits that limit the battery life. This effect is depicted in Figure 5.12.

The effect of DOD on cycle life is shown in Figure 5.13 for a cell with sintered electrode technology (at the 1-hour rate). Only about 700 cycles can be obtained with 100% DOD, while about 4000 cycles can be obtained with 25% DOD. In portable devices it is impossible to fix the DOD, as the use may be highly variable from shallow to complete discharges.

In case of repetitive shallow discharges, the so-called memory effect (or voltage depression) may appear. The cell, after recharge, may not be able to give its full capacity as if remembering the previous shallow discharges. Full capacity may be regained with some deep discharges followed by complete charges. In addition to a lower capacity, a lower voltage (100-150 mV) is observed.



This effect varies according to the cell technology, and tends to be modest in modern batteries to the point that most users never get to know it. A similar effect can be observed with long-term overcharge, especially at high temperatures. The rationale for the memory effect has long been debated. Its presence in Ni-MH cells too allows excluding the Cd electrode. According to some authors, the positive electrode is responsible as, in the conditions described above,  $\beta$ -NiOOH changes into  $\gamma$ -NiOOH [40].

Sealed Ni-Cd cells can be produced in a variety of types with different features. In Table 5.5, the characteristics of spirally wound batteries are presented.

The applications are also quite differentiated and include the following [39]:

Calculators	Cassette players and recorders
Dictating machines	Digital cameras
Instruments	Personal pagers
Photoflash equipment	Portable communications equipment
Portable hand tools and appliances	Portable computers
Radio control models	Radios
Tape recorders	Shavers
Toothbrushes	Television sets

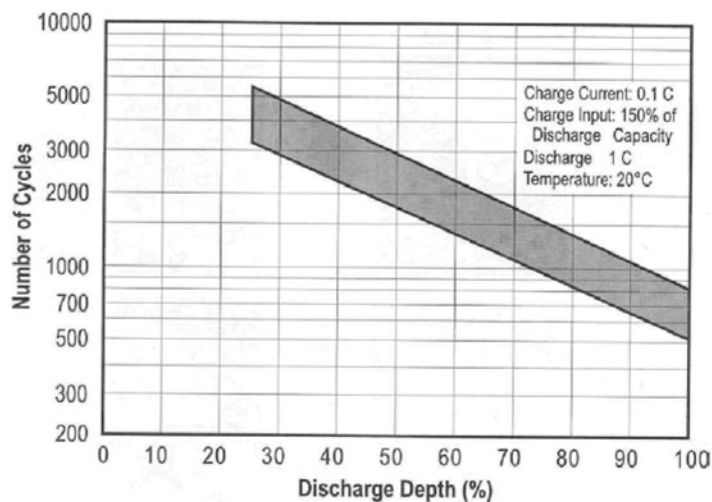


Figure 5.13. Number of cycles of a Ni-Cd battery (sintered technology) vs. DOD. (From Ref. 37)

Table 5.5. Spirally Wound Nickel-Cadmium Batteries. (Courtesy of Eagle-Picher Technologies)

Std Size	Nominal Capacity (mAh)	Diameter (mm) $\pm 0.2$	Height (mm) $\pm 0.3$	7 Hour Charge (mA)	1.5 Hour Charge (mA)	Approx. Weight (grams)
2/3AAA	200	10.0	28.4	40	200	6
AAA	300	10.0	44.4	60	300	11
2/3AA	300	13.9	28.5	60	300	13
2/3AA	400	13.9	28.5	60	400	14
4/5AA	700	13.9	42.5	140	700	20
4/3AA	1100	13.9	65.0	220	1100	30
AA	600	13.9	50.0	120	600	22
AA	700	13.9	50.0	140	700	22
AA	800	13.9	50.0	160	800	23
AA	900	13.9	50.0	180	900	24
AA	1000	13.9	50.0	200	1000	24
2/3A	600	16.5	27.2	120	600	20
4/5A	1200	16.5	42.2	240	1200	28
A	1400	16.5	48.2	270	1400	32
4/3A	1600	16.5	66.2	320	1600	41
2/3Sc	600	21.9	26.0	120	600	25
4/5Sc	1000	21.9	33.5	200	1000	40
Sc	1300	21.9	42.5	260	1300	45
Sc	1500	21.9	42.5	300	1500	46
Sc	1700	21.9	42.5	340	1700	47
4/3Sc	2200	21.9	49.5	440	2200	58
2/3C	1000	25.2	30.5	200	1000	46
C	2000	25.2	49.2	400	2000	63
C	2500	25.2	50.5	500	2500	70
D	4000	32.2	61.3	800	4000	140
D	4500	32.2	61.3	900	4500	145
3/2D	7000	32.2	90.0	1400	3500	195

With time, the use of these batteries in portable devices has been decreasing in favor of Ni-MH and Li-ion batteries, but in portable AV

equipment, power tools and cordless phones Ni-Cd batteries are still largely used. In particular, the industry appreciates their tolerance to overdischarge (below 1.0 V).

The environmental problems posed by the components of Ni-Cd batteries will be dealt with in Chapter 9.

## 5.4. Nickel-Metal Hydride Batteries

Many of the characteristics of sealed Ni-MH batteries are similar to those of the corresponding Ni-Cd batteries. However, the former have a higher energy density and a longer service life. In addition, the Ni-MH battery is more environmentally friendly as it does not contain cadmium. In Table 5.6, a comparison of the features of Ni-Cd and Ni-MH batteries is done [41].

The superior discharge capacity of the Ni-MH battery vs. Ni-Cd is shown in Figure 5.14. At the typical 0.2C rate, the former delivers 40% more capacity, and a correspondingly higher energy density. Thanks to the many design similarities between the two batteries, the user asking for more energy may easily replace a Ni-Cd battery with a Ni-MH one.

### 5.4.1. Materials and Electrode Reactions

The negative Cd electrode is replaced by a hydrogen storage alloy in the Ni-MH system. During charge, a hydrogen atom, formed by  $\text{H}_2\text{O}$  reduction, deposits on the surface of the alloy and then diffuses into it to form a metal hydride (MH). The reversible reactions can be written as:



The reaction at the positive electrode is the same occurring in a Ni-Cd battery. The electrolyte solution (aqueous KOH) is also the same.

The overall process consists in the reversible transfer of a proton from an electrode to the other. This is depicted in Figure 5.15. The proton released from the storage alloy during discharge is first taken by  $\text{OH}^-$  groups to form  $\text{H}_2\text{O}$  and, then, transferred to NiOOH to form  $\text{Ni(OH)}_2$ . The process is reversed upon charge. Therefore, the Cd electrode, where the reaction proceeds through a

Table 5.6. Comparison of sealed Ni-Cd and Ni-MH batteries. (From Ref. 41)

Application Feature	Comparison of Ni-MH to Ni-Cd Batteries
Nominal Voltage	Same (1.25V)
Discharge Capacity	Ni-MH up to 40% greater than Ni-Cd
Discharge Profile	Equivalent
Discharge Cutoff Voltages	Equivalent
High Rate Discharge Capability	Effectively the same rates
High Temperature (>35°C) Discharge Capability	Ni-MH slightly better than standard Ni-Cd cells
Charging Process	Generally similar; multiple-step constant current with overcharge control recommended for fast charging Ni-MH
Charge Termination Techniques	Generally similar but Ni-MH transitions are more subtle. Backup temperature termination recommended.
Operating Temperature Limits	Similar. Cold temperature fast charge limit is 10-15°C for both.
Self-Discharge Rate	Ni-MH higher than Ni-Cd
Cycle Life	Generally similar, but Ni-MH is more application dependent.
Mechanical Fit	Equivalent
Mechanical Properties	Equivalent
Selection of Sizes/Shapes/Capacities	Ni-MH product line more limited
Handling Issues	Similar
Environmental Issues	Reduced with Ni-MH because of elimination of cadmium toxicity concerns

dissolution-precipitation mechanism, is replaced by an electrode where a smooth solid-state process occurs, *i.e.*  $H^+$  uptake/release. This eliminates negative changes occurring during the life of the Cd electrode in its crystallography, mechanical integrity, surface morphology and electrical conductivity.

Furthermore, at variance with the overall reaction of the Ni-Cd system (page 84) where  $H_2O$  is consumed on discharge and reformed on charge, here there is no net reaction involving  $H_2O$ , so that the concentration and conductivity of the solution does not change. These favourable features are counterbalanced, as detailed in the following, by a lower power density, faster self-discharge and less tolerance to overcharge.

As in the case of the Ni-Cd battery, the Ni-MH battery can be subjected to overcharge and overdischarge with well identified reactions, as reported in the scheme of Figure 5.16 [36]. The cell capacity is limited by the positive electrode, with a negative to positive ratio of 1.5-2. During overcharge,  $O_2$  is evolved at the positive and diffuses to the negative to form  $H_2O$ . During overdischarge,  $H_2$  is evolved at the positive and again gives rise to  $H_2O$  at the negative. Therefore, at variance with the Ni-Cd battery, both  $H_2$  and  $O_2$  recombine to form  $H_2O$ , thus assuring sealed operation of the Ni-MH battery.

The alloys currently used are of the  $AB_5$  or  $AB_2$  type. An example of the former is  $LaNi_5$ , while  $ZrV_2$  exemplifies the second. Both types of alloys have undergone over the years important developments to improve their characteristics, which can be summarized as [42]: wide operating temperature range, high capacity and energy, long cycle life, high electrochemical activity,

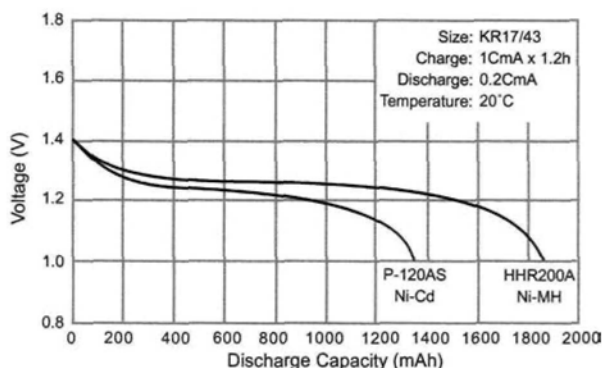


Figure 5.14. Comparison of the discharge capacity of similar Ni-Cd and Ni-MH batteries at 0.2C. (Courtesy of Panasonic)

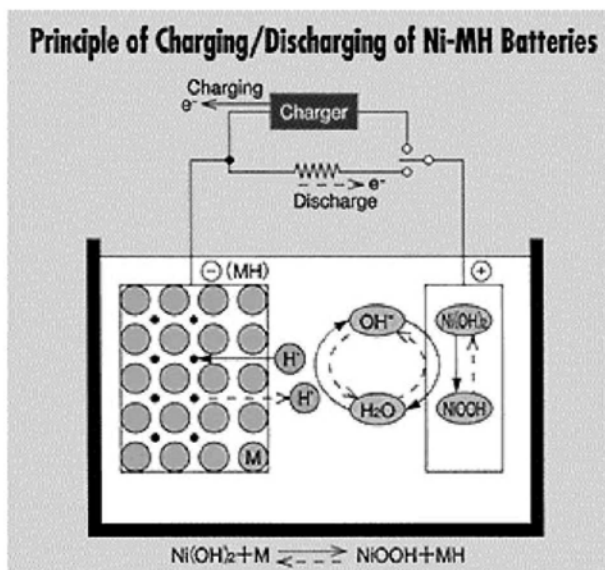


Figure 5.15. Principle of the charge/discharge process of a Ni-MH cell. The hydrogen ion moves back and forth between the two electrodes. (Courtesy of Toshiba)

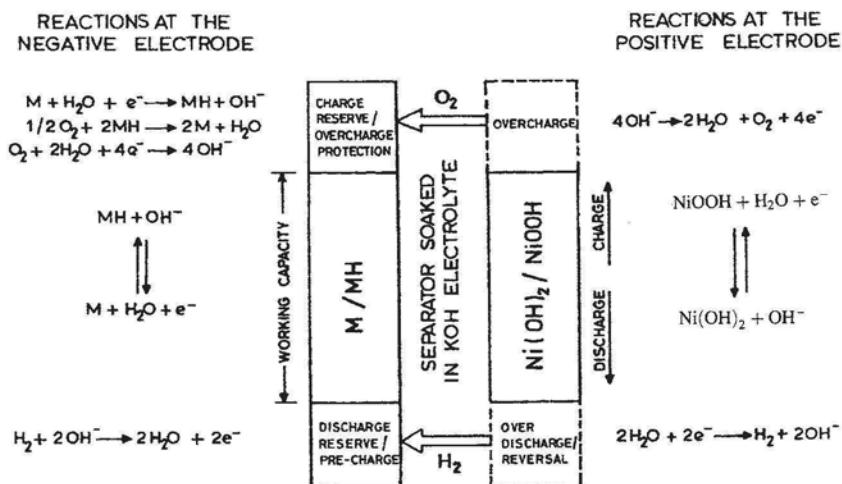


Figure 5.16. Scheme of all reactions occurring in a sealed Ni-MH cell. (From Ref. 36)

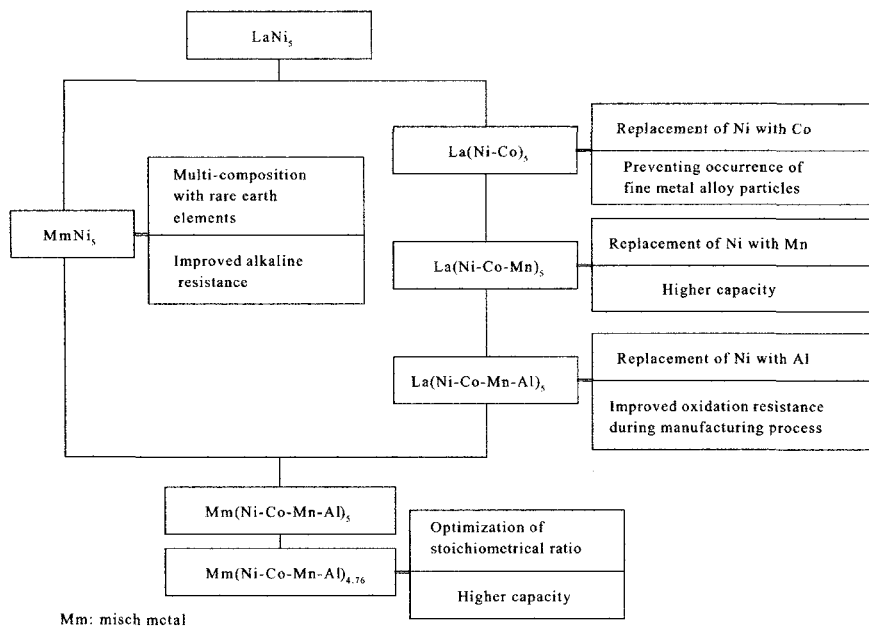


Figure 5.17. Progressive optimization of the  $AB_5$  hydrogen storage alloy for the negative electrode of a sealed Ni-MH battery. (From Ref. 38)

high hydrogen diffusion velocity, low cost, environmental friendliness. The scheme of Figure 5.17 presents the various optimization steps for the  $LaNi_5$  alloy [38]. Mm stands for misch metal, *i.e.* a naturally occurring mixture of rare earth elements: La, Nd, Pr, Ce. The composition currently used, *i.e.*  $Mm(Ni-Co-Mn-Al)_{4.76}$  gives a discharge capacity of 330 mAh/g, that is 10% higher than  $AB_5$ . Among the  $AB_2$  alloys, the one containing Ti, Zr, V, Ni and Cr has been found of particular interest, as it has a higher capacity. However, at low and high temperatures and demanding discharge rates, the  $AB_5$  alloy works better. As it is also cheaper and easier to use, this alloy is still preferred in sealed Ni-MH batteries.

A larger capacity is expected from new alloys under study. The *bcc* type (example:  $V_3Ti$ ) has twice the capacity of  $AB_5$ , and the *Mg-Ni* type (example:  $Mg_2Ni+2Ni$ ) has 1.5 times the capacity of  $AB_5$ . However, these new alloys share non-secondary drawbacks: poor corrosion resistance, shorter cycle life, initial activation and lower operating voltage (in comparison with  $AB_5$ ). Capacities of 700-1000 Ah/kg are thought possible in the future [43].

The performance of Ni-MH batteries also depends on the cathode formulation and on the nature of the separator. Addition of  $Co(OH)_2$  to the

cathode produces a Co oxide with a much higher conductivity than NiOOH [38]. The addition of  $Y_2O_3$  has also been found useful in increasing the utilization of the positive [44].

$O_2$  evolved at the positive on overcharge may oxidize the separator. Therefore, a chemically stable separator is needed as, for instance, sulfonated polypropylene.

#### 5.4.2. Cell Construction and Performance

Sealed Ni-MH batteries are constructed with the same designs of the Ni-Cd ones. The electrodes have high surface area so to stand high current rates. In the cylindrical configuration, the positive electrode has generally a felt or foam substrate, into which the active material is impregnated or pasted. The negative electrode has also a porous structure (perforated Ni foil or grid) supporting the plastic-bonded hydrogen storage alloy. The electrodes are spirally wound, as in the analogous Ni-Cd batteries, and stuffed into a Ni-plated steel can (see Figure 1.7c). The cell top contains, in this case too, a releasable safety vent, which operates at around 27 atmospheres.

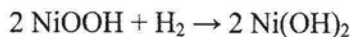
The prismatic batteries are mainly of the thin design for powering tiny devices. A better space utilization allows prismatic batteries to deliver up to 20% more capacity. The electrodes are flat and rectangular, other things being the same as in the cylindrical design (Figure 5.18)

In Figure 5.19, discharge curves of a cylindrical Ni-MH cell are shown at different rates. The cell loses little capacity by increasing the rate, although at the expenses of the mean voltage. At variance with the exothermic nature of the discharge reaction of Ni-Cd batteries, in these ones the discharge is endothermic. Therefore, heating due to the current flowing in the cell is partly balanced. Although a Ni-MH battery is capable of sustaining high discharge currents, repeated discharges at these currents reduce the battery's cycle life. Best results are achieved with rates of 0.2C to 0.5C.

The effect of temperature on discharge capacity is shown in Figure 5.20. Clearly, the temperature range outside  $0^{\circ}$ - $40^{\circ}C$  should not be used for optimum performance. In particular, the drop at low temperatures is due to the increase of the internal resistance.

The battery sensitivity to temperature is also evident in storage conditions. Capacity loss is rather fast at high temperatures, as shown in Figure 5.21. Self-discharge is due to the reaction of  $H_2$  released by the alloy with the positive electrode, and to slow decomposition of the latter, according to the reactions:





The first of these reactions is obviously influenced by the capacity of the alloy to hold hydrogen. In this respect,  $\text{AB}_2$  alloys are better than  $\text{AB}_5$ .

Room temperature storage does not produce a permanent capacity loss, as

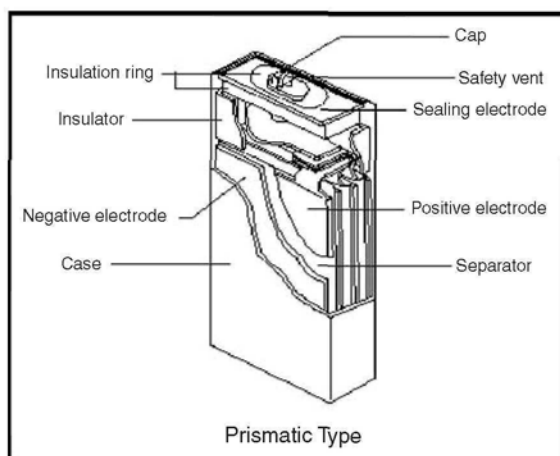


Figure 5.18. Construction of a thin prismatic Ni-MH battery. (Courtesy of Panasonic)

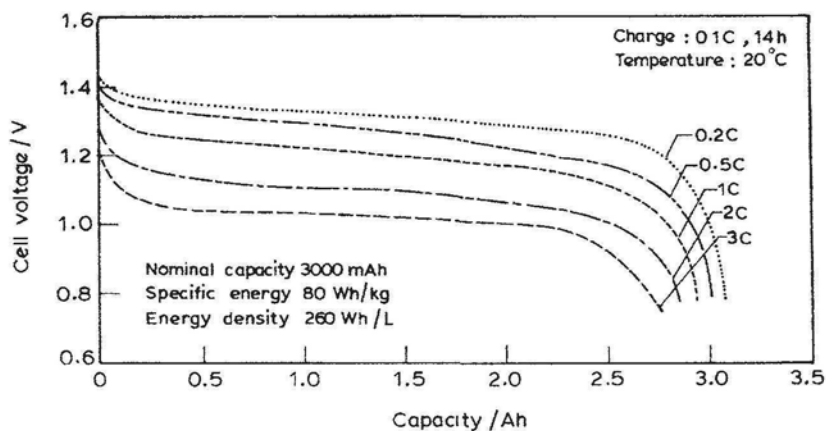


Figure 5.19. Discharge curves at various rates of a cylindrical 3-Ah cell. (From Ref. 36)

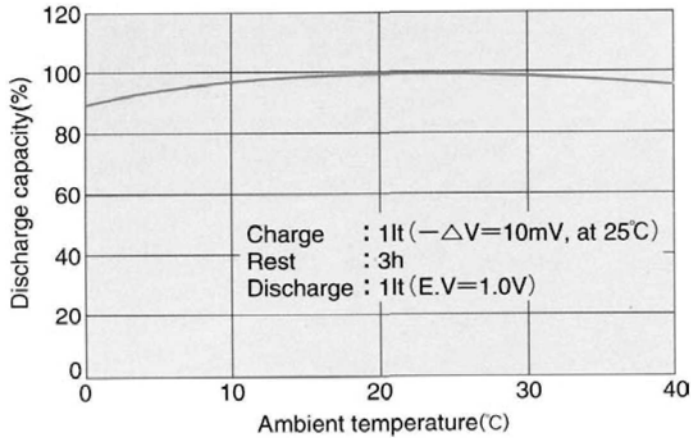


Figure 5.20. Effect of temperature on the discharge capacity of a sealed Ni-MH cell. (Courtesy of Sanyo)

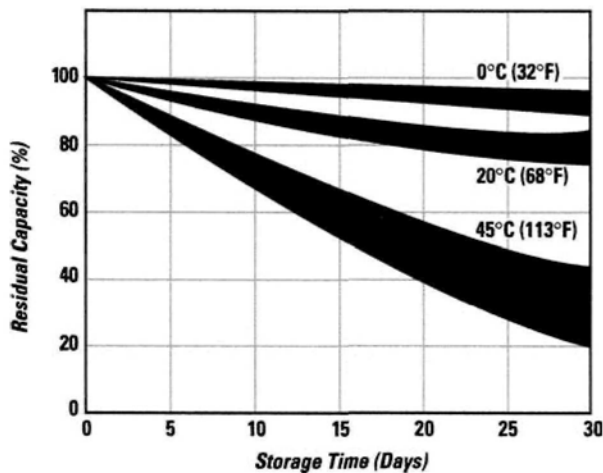


Fig 5.21. Storage characteristics of Ni-MH batteries at various temperatures. Charge at 0.3C for 5 hours; discharge at 0.2C to 1.0 V (room temperature). (Courtesy of Duracell)

full capacity is recovered upon charge. However, long term storage at high temperatures produces permanent damages to seals and separator, and should be avoided. Some tests have shown that continuous exposure to 45°C reduces the cycle life by 60% [45].

If one compares the curves of Figure 5.21 with the analogous curves for Ni-Cd batteries (Figure 5.9), the faster self-discharge of Ni-MH is evident at 45°C and at the same discharge rate. A Ni-Cd battery can still retain 60-70% of its capacity after one month, while a Ni-MH one delivers 20-40% only.

### 5.4.3. Charging the Ni-MH Battery

Charge is a critical step in determining the performance and overall life of Ni-MH batteries, due to their sensitivity to the charging conditions. It is of the utmost importance choosing the appropriate charging rate, the temperature range and the most effective techniques indicating end-of-charge.

Ni-MH batteries are commonly charged at constant current. The current values have to be limited to avoid overheating and incomplete O<sub>2</sub> recombination. Shapes of the charge curves at different rates (already introduced in Figure 1.4) are presented in Figure 5.22 together with the corresponding temperatures. The voltage raises more sharply around 80% charge, due to a more significant O<sub>2</sub> evolution, and tends to level off or to a maximum value at medium-high rates. In comparison with the charge of Ni-Cd batteries (Figure 5.10), the voltage drop, when present, is not so evident.

The charge process is exothermic in Ni-MH, while it is endothermic in

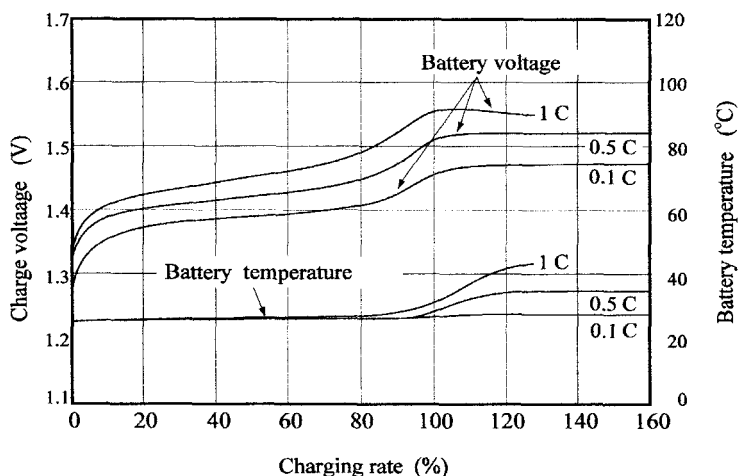


Figure 5.22. Voltage and temperature profiles of Ni-MH batteries charged at various rates. (From Ref. 38)

Ni-Cd. Therefore, the temperature of the former rises more quickly during charge and, for the same charge input, is higher than that of the latter. After about 80% charge, simultaneously with the  $O_2$  evolution, the temperature of both batteries sharply increases due to the exothermic  $O_2$  recombination reaction. This increase in temperature causes the voltage to drop (or level off) as the battery reaches full charge and enters the overcharge zone [46].

On the basis of the above considerations, the charge temperature has to be controlled to obtain a high discharge capacity. As shown in Figure 5.23, the temperature should not overcome  $30^\circ\text{C}$ , as an increasing  $O_2$  evolution takes places at high temperatures. On the other hand, it has been ascertained that the charge efficiency is very good in the range  $10\text{--}30^\circ\text{C}$ , so temperatures below  $10^\circ\text{C}$  should also be avoided.

Voltage drop and temperature rise, in addition to calculation of the charge input (Ah), can be taken as indicators of the end of charge, but, as can be inferred from the above discussion, the choice of the method greatly depends on the conditions of a specific charge. The need of a charge control is especially evident in fast charges, where temperature and pressure may reach exceedingly high values with possible cell venting. Hereafter, the methods for charge control are summarized.

**Charge input.** From current and time, the charge in Ah is calculated. This method can be applied only to slow charges ( $<0.3\text{C}$ ) to avoid overcharges that

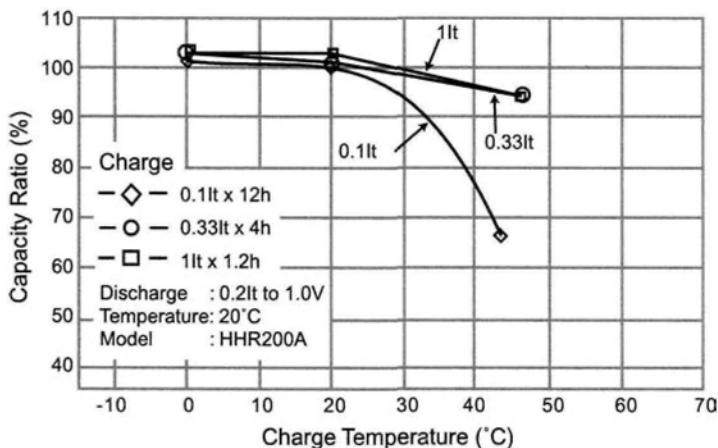


Figure 5.23. Effect of different temperatures (at three rates) on the capacity recoverable on discharge (at  $0.2\text{C}$ ). (Courtesy of Panasonic)

could occur in incompletely discharged cells.

*Voltage drop ( $-\Delta V$ ).* This method, obviously applicable if the drop is present, that is at high rates (and low temperatures), should stop charging at potentials of 5 to 10 mV past the peak. It is shown in Figure 7.13.

*Voltage plateau.* This is applicable to low-rate charges where the voltage levels-off (see charge at 0.1C in Figure 5.22). A top-up charge, *i.e.* a time- and current-limited charge, may follow to ensure full charge.

*Temperature cut-off (TCO).* This method stops charging when the temperature reaches a pre-set limit indicating overcharging. It is usually used as a backup of other methods, in case of their failure.

*$\Delta TCO$ .* This method measures the temperature increase with respect to the starting value. The limit temperature depends on several factors and, in particular, should be determined for each battery type. At the 1C rate, a typical  $\Delta TCO$  could be 15°C.

*Rate of temperature increase ( $\Delta T/\Delta t$ ).* This measures the rate of temperature rise vs. time (Figure 7.14) and stops the charge when a predetermined value, *e.g.* 1°C/min, is reached. This is the preferred method to stop high-rate charges, as it ensures longer cycle lives, as shown in Figure 5.24, in comparison with  $-\Delta V$ . Indeed, it can sense starting of overcharge earlier than the  $-\Delta V$  method. This confirms that the Ni-MH battery suffers if repeatedly overcharged.

In terms of charge rates, appropriate termination methods are described in Table 5.7 [47]. In general, one of these procedures can accomplish charging the Ni-MH battery.

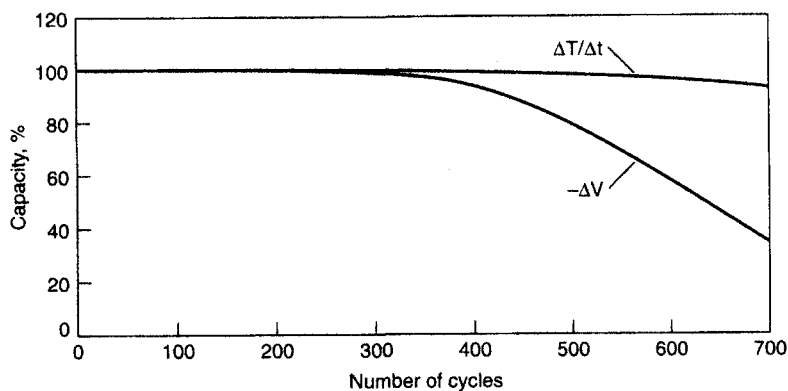


Figure 5.24. Influence of the charge termination method on cycle life and capacity of a sealed cylindrical Ni-MH cell. Charge rate: 1C, rest 0.5 h; discharge rate: 0.2C to 1.0 V, rest 2 h. Temperature: 21°C. (From Refs. 46, 47)

Table 5.7. Recommended charge termination methods as a function of charge rate. (From Ref. 45)

Charge Rate	Termination Method
1C to 0.5C	Voltage or temperature based
0.5C to 0.33C	Voltage based
0.33C to 0.1C	Not recommended
0.1C or below	Time limited

*Low-rate charge (12 hours).* If there is no need to charge a battery in a short time, a 12-hour charge at 0.1C may be adequate. A 120% charge input is ideally suited to ensure a long cycle life. The temperature range is 0-40°C, preferably 15-30°C.

*Quick charge (4 hours).* This requires charge control to avoid exceeding the O<sub>2</sub> recombination rate and overheating. A convenient rate may be 0.3C and termination may be controlled with  $\Delta V = -10$  mV. Termination backup methods: charge input of 120% and TCO of 60°C. The temperature range is 10-45°C. A top-up charge is not necessary.

*Fast charge (1 hour).* For obtaining the highest capacity in a fast charge, the following three-step procedure is recommended:

1. Charging at 1C with  $\Delta T/\Delta t$  termination (1°C/min) in the preferred temperature range 10-35°C.
2. Applying a top-up charge at 0.1C for half an hour.
3. Applying a maintenance (or trickle) charge at C/300 with no time limits.

The last step counterbalances self-discharge and is only required in applications with batteries in a fully charged state.

Recently, a battery producer (Rayovac) has introduced into the market a Ni-MH battery with built-in pressure control. This battery and its dedicated charger are said to allow battery charging in 15 minutes and up to 1000 times [48].

#### 5.4.4. Cycle and Battery Life

Some of the factors determining the battery life, *i.e.* temperature, current, storage, charge termination method, over-charging and -discharging, have been discussed above. Under proper conditions of use, *i.e.* charge/discharge at 0.2C, 20°C, limited overcharge, the Ni-MH battery can deliver in excess of 500 cycles before its capacity drops to 80% of the initial value.

Temperature is particularly important for the Ni-MH battery. Repeated charge/discharge cycles above 20°C cause a severe reduction in cycle life, as shown in Figure 5.25. Operation at high temperature, especially in the charged state, may cause excessive gas production and venting. On the other hand, low temperatures (below 0°C) impair the O<sub>2</sub> recombination process and, again, venting is possible.

The DOD is also very important. Cycling at moderate rates and 100% DOD can still allow obtaining ~500 cycles. However, on repeated deep cycles at high currents, the performance starts to deteriorate after 200-300 cycles. Shallow rather than deep discharge cycling should be applied at these currents. Several thousand cycles have been reported with a 40%DOD at 0.6C discharge rate [36]. Battery life is affected by the same factors determining the cycle life. In particular, temperature plays a fundamental role. In Table 5.8, the recommended and permissible temperature ranges for charge, discharge and storage are summarized.

#### 5.4.5. Battery Types and Applications

In Table 5.9, examples of commercial cylindrical Ni-MH cells are reported. Their capacity is well superior to that of the corresponding Ni-Cd

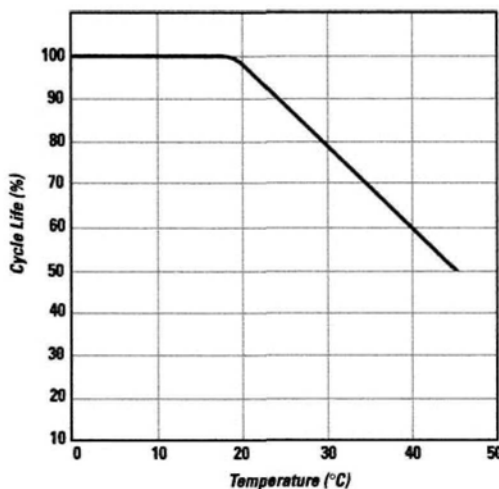


Figure 5.25. Effect of repeated cycling at various temperatures on the cycle life of Ni-MH batteries. Charge and discharge at 0.25C. (From Ref. 47)

Table 5. 8. Recommended and permissible temperature ranges for operation and storage of sealed Ni-MH batteries. (From Ref. 47)

Condition	Recommended	Permissible
Low Rate Charge	15°C to 30°C	0°C to 45°C
Quick Charge	10°C to 30°C	10°C to 45°C
Fast Charge	10°C to 30°C	10°C to 45°C
Trickle Charge	10°C to 30°C	10°C to 35°C
Discharge	0°C to 40°C	- 20°C to 50°C
Storage, Short Term	10°C to 30°C	- 20°C to 50°C
Storage, Long Term	10°C to 30°C	- 20°C to 35°C

batteries. This corresponds, as already stated, to a higher energy. These batteries have now specific energies approaching 100 Wh/kg and energy densities above 300 Wh/L. However, continuous material improvements are expected to further increase these values. The memory effect is barely noticeable in today's Ni-MH cells as the corresponding capacity loss is well below 5% of the total capacity: the user can hardly become aware of this effect.

Due to its higher energy, the Ni-MH battery has substituted the Ni-Cd one in several high-end portable devices, with some exceptions in high-drain power tools and applications where battery cost is of prime importance. Typical applications include the following: cellular phones, personal handy phone system (PHS), notebooks, PDAs, camcorders, portable audio and video equipment, measuring instruments, medical equipment.

## 5.5. Rechargeable Alkaline Zn/MnO<sub>2</sub> Batteries

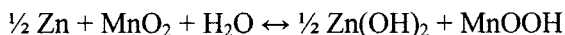
These batteries have the same chemistry and design of primary alkaline batteries (Section 4.3). Zn powder is the negative electrode, MnO<sub>2</sub> the positive electrode, and aqueous KOH the solution. The cells have a cylindrical shape and the active materials are set in the can according to the bobbin type (inside-out) configuration (see Figure 4.4).



Table 5.9. Commercial cylindrical Ni-MH cells. (Courtesy of GP Batteries)

Nickel Metal Hydride Series - Cylindrical Type										
Cell Size	Model No.	Nominal Voltage (V)	Capacity (0.2C discharge) (mAh)		Nominal Dimension (mm)		Weight (g)	Standard Charge		1 Hr Charge Current (mA)
			Minimum	Typical	Diameter (D)	Height (H)		Current (mA)	Time (hour)	
High Capacity Series										
AAA	GP65AAAHC	1.2	630	650	10.5	44.5	13	65	14	650
	GP70AAAHC		680	700				70		700
	GP75AAAHC		730	750				75	16	750
	GP80AAAHC		780	800				80		800
AA	GP130AAHC	1.2	1250	1300	14.5	50	26	130	14	1300
	GP170AAHC		1650	1700				170		1700
	GP180AAHC		1750	1800				180		1800
	GP200AAHC		1900	2000				200		2000
C	GP350CHC	1.2	3500	3700	25.8	50	78.5	350	14	3500
D	GP700DHC	1.2	7000	7350	33	61.5	170	700	14	7000
Standard Series										
AAA	GP60AAAHC	1.2	600	630	10.5	44.5	13	60	14	600
AA	GP60AAHC	1.2	600	660	14.5	50	16	60	14	600
	GP130AAHC	1.2	1300	1400			26	130		1300
C	GP220CH	1.2	2200	2300	26.2	50	47	220	14	2200
D	GP220DH	1.2	2200	2300	33	61.5	47	220	14	2200

The total cell reaction is:



The reaction at the positive electrode is a one-electron process, *i.e.* insertion/release of  $\text{H}^+$  into/from the tunnels of the  $\text{MnO}_2$  molecule without nucleation of a new phase. To avoid the reduction of  $\text{MnO}_2$  below the  $\text{MnOOH}$  state (overdischarge), the cell capacity is limited by the Zn electrode. Instead of pure  $\text{MnO}_2$ , a doped form containing 10%  $\text{Bi}_2\text{O}_3$  may be used. The latter allows Mn reversible reduction from the tetra- to the di-valent state, with consequent capacity increase [49].

At variance with the positive in the primary cell, the positive of the rechargeable one contains (in addition to graphite for reducing the electrode resistance)  $\text{BaSO}_4$  to increase capacity and improve cycling, and a silver catalyst. The latter recombines the hydrogen formed by Zn corrosion.

The Zn powder contains gelled KOH and is placed in the can centre, around a nail as a current collector. The separator is regenerated cellulose with a high resistance to the caustic solution.

The cell has an initial voltage of 1.5 V and can be discharged to 0.8 V. When recharged, the voltage limit is 1.65-1.68 V, otherwise  $\text{Mn}^{\text{VI}}$  and  $\text{O}_2$  are formed, with subsequent capacity losses. The rechargeable battery has a capacity in the first cycle corresponding to 70-80% of the primary battery. On subsequent cycling, the capacity decreases and the overall cycle life depends to a large extent on the DOD: shallow discharges can produce 200 cycles or more, while 100% discharges limit the cycle life to some 20 cycles. In figure 5.26, 100% DOD cycles are shown. The capacity drops to 50% of the initial one after 20 cycles. Recent improvements are reported to prolong the cycle life to 50 cycles.

Shallow cycling (~25% DOD) is presented in Figure 5.27. The discharge voltage continuously drops as cycling goes on, and the final cut-off voltage has to be set at ~1 V to reach 200 cycles.

To obtain the longest cycle life, the rechargeable alkaline cell should be recharged after each discharge. Recharging can be done with one of these techniques:

- *Constant potential*: 1.65-1.68 V. A low, decreasing current in the mA range charges the cell in 10-12 hours.
- *Constant current*: this can only be applied if the voltage does not exceed 1.65 V to avoid cell venting. A shut-off control is necessary.
- *Pulses*: this technique allows charging in about 2 hours.
- *Overflow*: is applied to multicell batteries and relies on electronic control.

The cyclability of the Zn/ $\text{MnO}_2$  battery is impaired by low temperatures, due to the decreasing electrolyte conductivity. The AA-size performs better

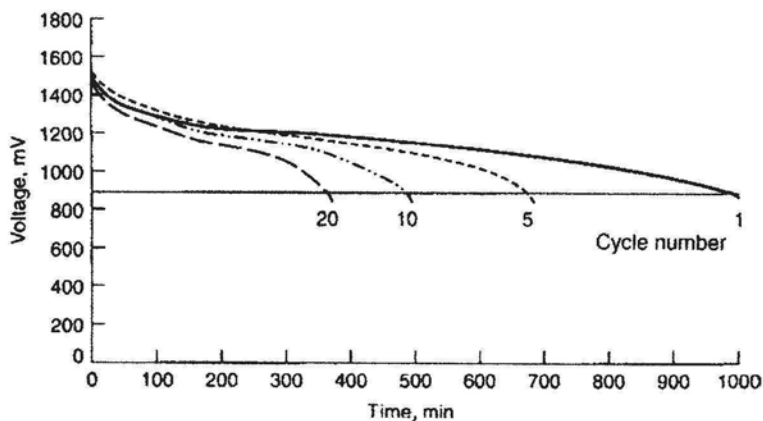


Figure 5.26. Cycling characteristics of an AA rechargeable Zn/MnO<sub>2</sub> cell on a 10-ohm load. (From Ref. 49)

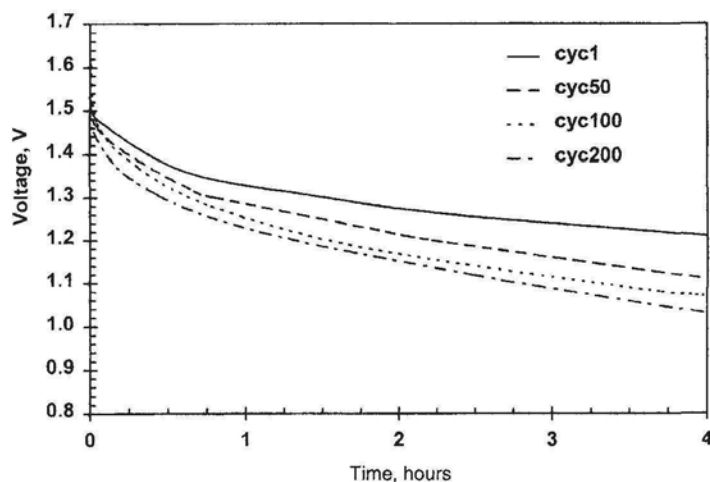


Figure 5.27. Cycling characteristics of an AA rechargeable Zn/MnO<sub>2</sub> cell discharged 4 hours/day on a 10-ohm load. (From Ref. 49)

than the D-size because of its thinner cathode. At high temperatures, the capacity is somewhat better thanks to the increased electrolyte conductivity and greater MnO<sub>2</sub> utilization.

An outstanding feature of alkaline rechargeables is their storage ability. In comparison with Ni-Cd or Ni-MH batteries, the capacity retention is much

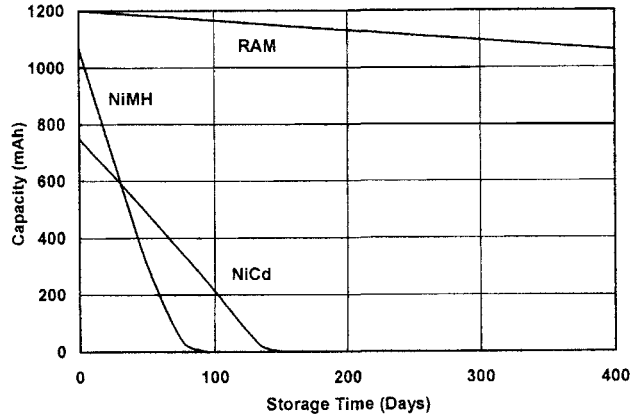


Figure 5.28. Self-discharge of Ni-Cd, Ni-MH and Zn/MnO<sub>2</sub> cells at 20°C. (From Ref. 50)

better, as shown in Figure 5.28 [50]. With respect to Ni-MH, the room-temperature self-discharge is ~100 times lower. Fresh cells can survive 4-5 years of storage.

Alkaline rechargeables are produced in only a few sizes: AAA, AA, C, D, and the so-called Bundle-C and Bundle-D. Bundle-C contains 2 AA cells in a C-size container, while Bundle-D contains 4 AA cells in a D-size container (the AA cells being connected in parallel). It has been ascertained that using such

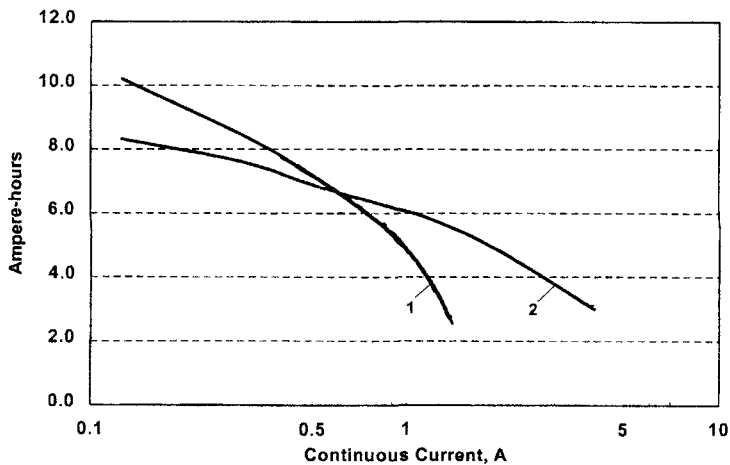


Figure 5.29. Comparison of the capacity vs. current drain for a Zn/MnO<sub>2</sub> D cell (1) and four AA cells in a D-size can (2). Cut-off at 0.9 V. (From Ref 49)

bundles allows a better performance in a cell with a lower weight. Figure 5.29 compares the rate capability of a D-size and a Bundle-D cell. Using the smaller AA cells, the Bundle-D cell has a higher electrode surface and a better rate capability.

Given the extreme variability of the capacity delivered by a cell as a function of DOD, discharge rate and cycle number, it is difficult to assign to this system values of energies. A specific energy of  $\sim 100$  Wh/kg has been reported for the initial discharge of an AA cell at C/15.

Rechargeable Zn/MnO<sub>2</sub> batteries can obviously replace the corresponding primaries. In a general consumer usage with relatively deep cycles ( $\sim 80\%$  DOD), the replacement factor is 20-25. At low-moderate drains, *e.g.* in toys, pagers, handheld games, *etc.*, a rechargeable battery is said to replace 100 primary batteries. Instead, its use is not recommended in power-demanding devices, such as digital cameras, computers, *etc.*

## 5.6. Rechargeable Lithium Batteries (with Li-Based Negative Electrodes)

As soon as the possibility of using a Li electrode in batteries with organic electrolytes was demonstrated, a frantic activity to develop rechargeable batteries started. However, the problems posed by the reactivity of Li with the electrolyte were immediately apparent. Freshly deposited Li is more reactive than bulk Li and tends to be encapsulated by electrolyte decomposition products, so becoming inactive. Due to the progressive loss of active Li, the charge/discharge efficiency remains well below unity and excess Li (3-4 times) has to be used with respect to the cathode capacity. Furthermore, Li can only deposit on the remaining active Li sites and grows in a dendritic form. With repeated cycling, dendrites can perforate the separator and reach the positive, thus shorting the cell.

In this section, the long story of all attempts made for building secondary cells based on the Li negative will not be told. The numerous positives, the various electrolytes (liquid or polymeric organic, and inorganic), and the additives aimed at improving Li cyclability can be found elsewhere [23,51,52]. Here, only systems that are commercially available (although in niche applications) or look especially prospective will be described.

Leaving aside the systems that have reached the stage of pilot plant, three of them have been commercialized and eventually withdrawn from the market. The first one, Li/TiS<sub>2</sub>, is important as its investigation, mainly carried out in the 1970s at the Exxon Laboratories, has allowed getting an inside in the process of Li<sup>+</sup> reversible intercalation into a host structure. This battery failed because it

could deliver only few cycles instead of the several hundreds expected. It disappeared so quickly that many consider Li/MoS<sub>2</sub> as the first real commercial system. This cell, developed by Moli Energy (Canada) in the mid-1980s with a cylindrical AA shape, survived few years before being withdrawn for safety reasons. The third system, Li/Li<sub>0.3</sub>MnO<sub>2</sub>, was commercialized by Tadiran (Israel) and used a special form of MnO<sub>2</sub> (to be dealt with later) and a particular electrolyte (LiAsF<sub>6</sub>-dioxolane) to prevent formation of Li dendrites. This battery was intrinsically safe, as a temperature increase to 125°C, due to a short circuit or any other abuse, caused solvent polymerization and shutdown because of the high internal resistance. Unfortunately, this battery could only be charged at low rates (<C/9), as at higher rates Li deposited in grains that reacted with the electrolyte.

At present, batteries commercialized are: Li/V<sub>2</sub>O<sub>5</sub>, Li/Li<sub>x</sub>MnO<sub>2</sub> and Li/Nb<sub>2</sub>O<sub>5</sub>. All of them use Li alloys with Al, instead of pure Li, as the negative electrode. Al improves storage characteristics and reduces formation of dendrites. However, a serious drawback with the formation of this alloy is the large volume expansion, which produces electrode pulverization and loss of electrical contact on prolonged cycling. For the end member Li<sub>9</sub>Al<sub>4</sub>, a volume change of 238% has been calculated [53]. Work carried out by Sanyo has shown that some additives, with special reference to Cr and Mn, are able to control the mechanical deterioration of the alloy [23,24]. The Li-Al alloy has a potential lower than that of pure Li by ~0.3 V. Its theoretical capacity is 0.8 Ah/g, vs. 3.86 for Li, but the latter requires, as already mentioned, a 3-4 times excess. Li-Al alloys cannot be extruded into thin foils and, so, can only be used as disks in coin cells. Indeed, all three batteries listed above are commercialized as coin (button) cells.

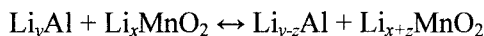
### 5.6.1. Li/Li<sub>x</sub>MnO<sub>2</sub> Batteries

This is the most important of the secondary batteries with the negative electrode based on Li.

The material for the positive electrode is obtained by partly lithiating MnO<sub>2</sub> with a convenient Li compound, *e.g.* LiOH, LiNO<sub>3</sub> or LiI, at an appropriate temperature. Much debate has been going on for years on the nature of the material so formed. According to some authors, it contains MnO<sub>2</sub> (in the crystallographic  $\gamma$ - $\beta$  form) and Li<sub>2</sub>MnO<sub>3</sub>; others believe that an orthorhombic phase, *e.g.* Li<sub>0.33</sub>MnO<sub>2</sub>, is formed; and, finally, the formation of a phase containing domains of lithiated  $\gamma$ -MnO<sub>2</sub> and low-temperature Mn spinel (stoichiometric spinel has the composition Li<sub>2</sub>MnO<sub>4</sub>) is suggested [54]. The similarity of the X-Ray patterns of the above compounds and the influence of

the synthesis conditions (temperature, time and lithiation mode) explain the different hypotheses.

Whatever its real nature, this lithiated Mn oxide features capacities of  $\sim 200$  mAh/g (active material only), a flat voltage of  $\sim 2.5$  V vs. Li-Al and a good cyclability. The overall reversible process can be described as:



$\text{Li}^+$  is inserted during discharge in the tunnels of the tri-dimensional structure of lithiated Mn oxide, and de-inserted on charge.

A typical discharge curve of a coin cell is shown in Figure 5.30. As these cells have self-discharges of 1-2%/year at room temperature, they can be used as received, *i.e.* without preliminary charge. The cycle life greatly depends on the DOD, as shown in Figure 5.31. A 100% DOD allows for 50 cycles, while a 20% DOD grants 500 cycles. These cells are typically used as backup power sources: the cell of Figure 5.30 can deliver 10  $\mu\text{A}$  for one year. Operating temperature range is:  $-20$ – $60^\circ\text{C}$ . As for the electrolyte, Sanyo reports excellent performance with the composition:  $\text{LiCF}_3\text{SO}_3$ -EC-BC-DME (see Section 4.7 for acronyms).

The rechargeable coin cells have the shape shown in Figure 4.11a for primary Li/MnO<sub>2</sub>. Their capacities range from 1 to 100 mAh at currents of 5 to 500  $\mu\text{A}$ . Charging is carried out with the constant voltage mode, *e.g.* 3.10 V. The charger contains a resistor to limit/control the current during the initial and final charge stages. Sanyo, Maxell and Panasonic include such batteries in their

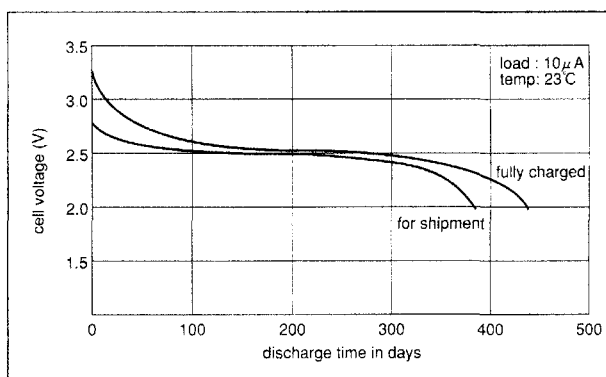


Figure 5.30. Discharge curves of a Li-Al/Mn oxide coin battery. Nominal capacity, 100 mAh. (Courtesy of Sanyo)

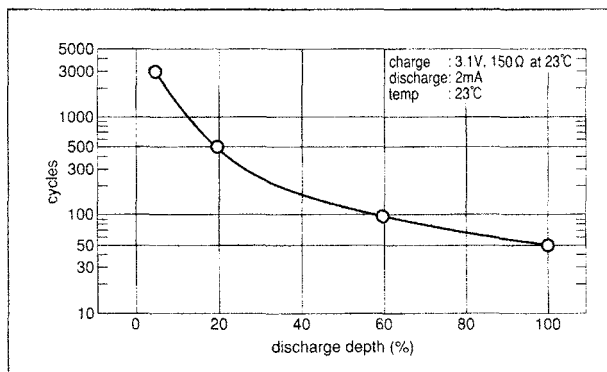


Figure 5.31. Cycle number vs. DOD for a Li-Al/Mn oxide coin battery. Nominal capacity 30 mAh. (Courtesy of Sanyo)

catalogs.

Devices in which these cells can be used include: PCs, PDAs, calculators, memory cards, timer-equipped home electronics, hybrid power sources in combination with solar cells, *etc.*

### 5.6.2. Li/V<sub>2</sub>O<sub>5</sub> Batteries

This battery has features similar to the one containing Mn oxide. However, the discharge curve is different with a typical two-step profile (the 1<sup>st</sup> at ~3 V and the 2<sup>nd</sup> at ~2.8 V), following Li<sup>+</sup> intercalation into the layered structure of V<sub>2</sub>O<sub>5</sub>.

This battery has excellent overcharge resistance. For instance, applying a continuous voltage of 3.5 V for 100 days at 60°C does not cause an appreciable effect on the discharge characteristics. Coin cells of capacities between 1.5 and 100 mAh are available (Panasonic) for the same applications listed for Li/Li<sub>x</sub>MnO<sub>2</sub> cells. The cycle life is about the same.

### 5.6.3. Li/Nb<sub>2</sub>O<sub>5</sub> Batteries

The positive of this cell is Nb<sub>2</sub>O<sub>5</sub> and, in this case, the Li<sup>+</sup> intercalation into its structure gives rise to an operating voltage of 1.2 V (nominal: 2 V). Li/Nb<sub>2</sub>O<sub>5</sub> cells are only produced as very thin coin cells of 1 or 4 mAh (Sanyo, Panasonic) for low-voltage memory backup. They are ideally suited for



applications using the newer technology, low-voltage integrated circuits, *e.g.* for cellular phones.

#### 5.6.4. Li/S Batteries

Sulphur can provide a specific capacity of 1675 mAh/g and a specific energy of 2600 Wh/kg in a Li/S cell, thus looking as a very appealing material for Li batteries. However, realization of an efficient electrode has been rather elusive for a long time, due to the low conductivity and high solubility of sulphur. In recent years, efforts to exploit its potentialities have been renewed and interesting results reported. Sulphur is reduced in two steps. During the first, at  $\sim 2.4$  V, several Li polysulphides are formed, *e.g.*,  $\text{Li}_2\text{S}_4$ ,  $\text{Li}_2\text{S}_8$ , *etc.*, while in the second step, at  $\sim 2.0$  V,  $\text{Li}_2\text{S}$  is formed (Figure 5.32). The polysulphides tend to dissolve and diffuse to the Li electrode where they are further reduced. The reduced forms may diffuse back to the positive where they are re-oxidized. This electrochemical shuttle prevents full recharge of the Li/S battery. Furthermore, the lower plateau has slow charge-discharge kinetics [55].

Development of Li anode protection from polysulphide attack leads to a shuttle reduction of 3 orders of magnitude and self-discharge of  $\sim 10\%$  per month. If anode protection is coupled with an improved electrolyte, 100% charge efficiency is achieved [55]. As a result, total sulphur utilization can reach 70% or 1200 Ah/kg. Addition of a catalyst to enhance the kinetics of the lower plateau affords 90% sulphur utilization, *e.g.* 1500 Ah/kg.

Various prototype Li/S cells with protected lithium anode and capacities ranging from 1.2 to 2.5 Ah have provided 250-300 Wh/kg and similar Wh/L

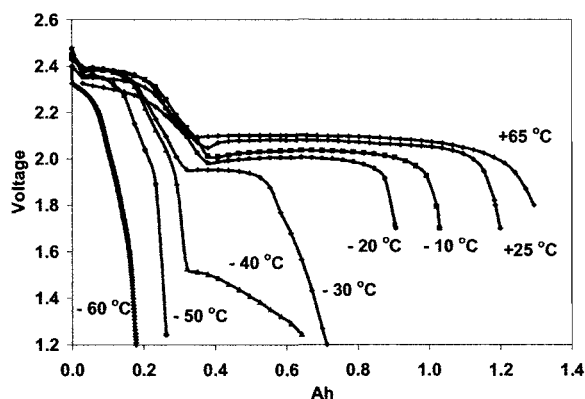


Figure 5.32. Discharge curves of a Li/S cell at various temperatures. (From Ref. 55)

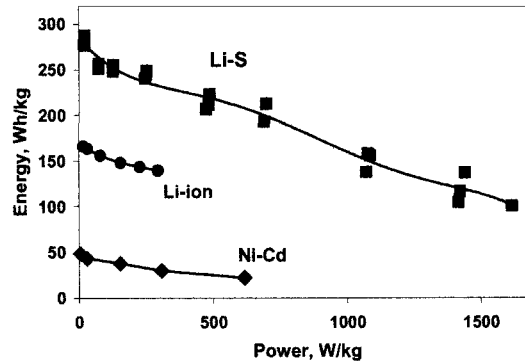


Figure 5.33. Ragone plot (energy vs. power) for prototype Li/S cells and Li-ion and Ni-Cd cells. (From Ref. 55)

values. The improved electrolyte (not yet disclosed) affords a high specific power, 2 KW/kg. As shown in Figure 5.33, prototype Li/S batteries can give higher specific energies than Li-ion and Ni-Cd batteries at any discharge power. The high rate capability is due to the fact that the active species (sulphides) are soluble and, thus, readily available for the electrochemical reactions.

At rather low temperatures, these Li/S batteries maintain a good percentage of the room temperature discharge capacity (Figure 5.32) and the charge too can be done at low temperatures.

This battery has been particularly developed in the U.S.A. by Sion Power Corp. and prototypes suitable for applications in portable devices are available for testing.

## 5.7. Lithium-Ion Batteries

The introduction of these batteries and the following developments represent a turning point in the advancement of all electronic devices, with a special reference to the portable ones. This is the result of a series of favourable characteristics:

- High specific energy and energy density
- Low self-discharge
- Long cycle life
- No maintenance
- No memory effect
- Fairly wide operation temperature
- Fairly high rate capability

- Possibility of miniaturization and very thin form factors.

On the other hand, some weak points also need to be mentioned:

- Relatively high initial cost
- Need of a protection circuit to avoid overcharge, overdischarge and excessive temperature rise
- Degradation at high temperature
- Lower power than Ni-Cd or Ni-MH, especially at low temperatures.

However, it is to be stressed that some of the above drawbacks are being progressively reduced: the cost is steadily decreasing, some Li-ion batteries (especially the polymeric ones) can work with simplified protection elements (see also Chapter 7), and the power output is getting better thanks to proper battery engineering. In the following, it will be shown how the user himself may contribute to get the best performance and the longest life by avoiding some adverse conditions, *e.g.* exposure to high temperatures and repeated deep discharges.

A Li-ion cell is based on two electrodes able to insert  $\text{Li}^+$  in their crystalline structure. The term insertion includes both bi- and tri-dimensional structures. In the case of bi-dimensional (layered) structures, the term intercalation is preferentially used. Intercalation positive electrodes have been known for quite some time. Sulphides, *e.g.*  $\text{MoS}_2$ ,  $\text{TiS}_2$  and  $\text{NbS}_3$ , or oxides, *e.g.*  $\text{V}_2\text{O}_5$ ,  $\text{V}_6\text{O}_{13}$  or  $\text{LiCoO}_2$ , had already shown in the 1970s and 1980s their capability of reversibly inserting  $\text{Li}^+$ . For this reason, the first attempts to substitute the Li metal as a negative electrode in rechargeable cells were also addressed to inorganic materials, such as  $\text{MoO}_2$  and  $\text{WO}_2$ . However, due to their poor cycling ability, these materials were abandoned, also in view of the emerging favorable characteristics of negatives based on carbons. At present, a vast majority of commercial Li-ion cells has C as a negative,  $\text{LiCoO}_2$  as a positive, and an organic liquid or polymeric electrolyte.

### 5.7.1. Carbons

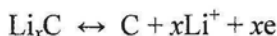
Carbons capable of  $\text{Li}^+$  intercalation can be roughly classified as graphitic and non-graphitic. Pure graphite has a layered structure with a perfect stacking of the graphene layers, *i.e.* is the basal planes formed by the hexagonal network of C atoms, and is highly crystalline. Graphitic carbons have a layered structure characterized by some structural defects. Some carbons may have a relatively high content of such defects or turbostratic disorder.

Non-graphitic carbons are characterized by amorphous areas together with more crystalline (graphitic) ones. These carbons may be divided into two classes: graphitizing (soft) carbons, *i.e.* those developing a graphitic structure by

heating at temperatures as high as 3000°C, and non-graphitizing (hard) carbons, *i.e.* those unable to assume a graphitic structure. This last feature is connected with the links between graphene layers (cross-linking), so that they are not free to move and stack one upon another, thus assuming a reasonable order. In Figure 5.34, a schematic view of the C layers arrangement in graphite, soft carbon and hard carbon is shown. All these carbons have received attention as candidates for Li-ion batteries. The initial choice of a soft carbon (coke), made by Sony for their first-generation batteries, later gave way to the use of graphite. Therefore, this type of carbon will be dealt with in more detail.

In pure graphite, the layers are stacked as shown in Figure 5.35. Graphite with this crystalline structure is called hexagonal graphite. A different ordering may also occur (rhombohedral graphite) but the former is prevalent [56]. Up to 1  $\text{Li}^+$  can be intercalated per 6 C atoms, *i.e.* the limiting composition is  $\text{LiC}_6$ . What happens to the structure when these  $\text{Li}^+$  ions are intercalated between the layers? There is a new ordering of the planes, in which two neighbouring layers directly face each other. In other words, the stacking sequence, A-B-A (Figure 5.35), converts to a sequence A-A-A (Figure 5.36A). The original interlayer distance increases (by about 10% in  $\text{LiC}_6$ ) while  $\text{Li}^+$  distributes as shown in Figure 5.36B.

The  $\text{Li}^+$  intercalation/de-intercalation reaction at the negative electrode can be described as:



Full  $\text{Li}^+$  intercalation into the graphite layers (charge) shifts the interlayer distance from 0.335 nm to 0.372 nm, and this expansion is fully reversed upon de-intercalation (discharge). In the long run, expansion/contraction cycles may be deleterious for the cyclability. However, optimization of the cell structure

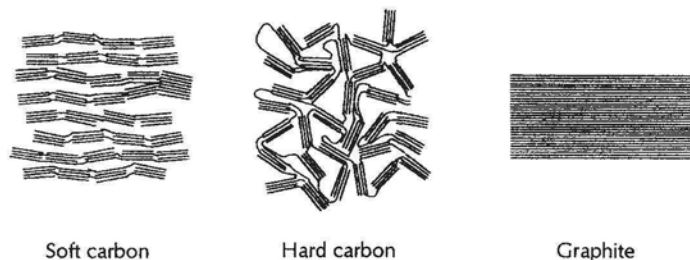
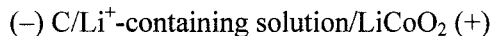


Figure 5.34. Carbon types showing different stacking of the carbon layers.

allows compensating for the electrode deformation, and graphite is now the most widely used negative in Li-ion cells.

If in a cell of the type:



a virgin C electrode is cathodically polarized so to intercalate  $\text{Li}^+$ , a preliminary electrolyte decomposition and formation of a layer on C occurs. A solid electrolyte interface (SEI) is built on the C surface in the so-called formation process. Such a process is necessary as the behavior of the C electrode depends on the characteristics of this layer. The 1<sup>st</sup> cycle (charge-discharge) of a graphite electrode is shown in Figure 5.37A. The initial voltage vs. a  $\text{Li/Li}^+$  reference electrode is above 3 V but drops suddenly to about 0.8 V, where electrolyte decomposition starts. The SEI formation continues down to  $\sim 0.2$  V; at this potential  $\text{Li}^+$  intercalation may begin. When the voltage approaches 0 V, the charge has to be stopped to avoid Li deposition on C, and the discharge ( $\text{Li}^+$  de-intercalation) starts. Because of the capacity needed for the SEI formation, the charge capacity exceeds the discharge capacity. The difference is called irreversible capacity and should obviously be kept to a minimum value to reduce excess of the  $\text{Li}^+$  source ( $\text{LiCoO}_2$  in this example) in a real battery.

The irreversible capacity largely depends on the surface area of the carbon material. The higher the surface area, the larger the electrolyte

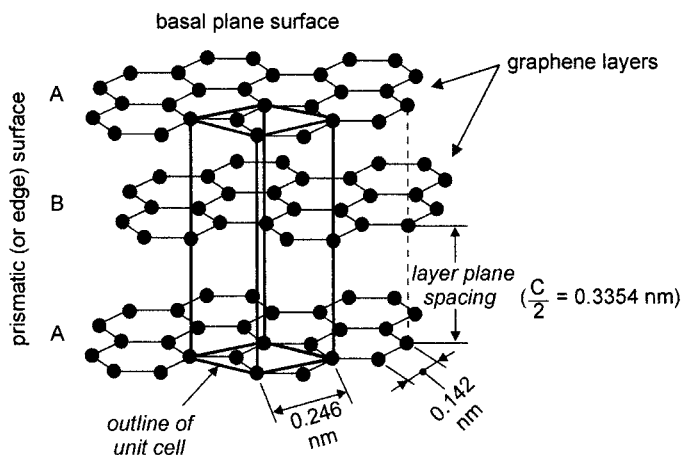


Figure 5.35. Crystal structure of hexagonal graphite showing the layer stacking sequence, the unit cell, and the interlayer space. (From Ref. 56)

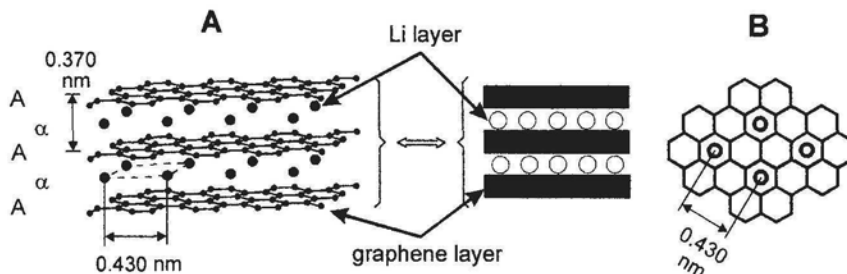


Figure 5.36. Layer stacking sequence and interlayer ordering of the intercalated lithium in  $\text{LiC}_6$  (A). In-plane structures of  $\text{LiC}_6$  (B). (From Ref. 56)

decomposition and, so, the irreversible capacity in the 1<sup>st</sup> cycle. This is a general rule for any positive or negative electrode in the presence of electrolyte that may undergo redox processes. For the specific behavior of graphite, the relationship between surface area and irreversible capacity is shown in Figure 5.38 [57]. A surface area below  $\sim 5 \text{ m}^2/\text{g}$  is recommended. Indeed, at  $5 \text{ m}^2/\text{g}$  the irreversible capacity is  $\sim 50 \text{ mAh/g}$ , that is 13% of the theoretical specific capacity of graphite for  $\text{LiC}_6$  ( $372 \text{ mAh/g}$ ). In last-generation cells, the irreversible capacity is kept below 10%, and surface treatment of graphite can reduce the loss to 7%.

Figure 5.37B shows the 1<sup>st</sup> cycle of a soft carbon (coke). The irreversible capacity is much the same as the one of graphite. However, it can be noted that the charge/discharge curves are more sloping, the voltage vs.  $\text{Li/Li}^+$  is higher

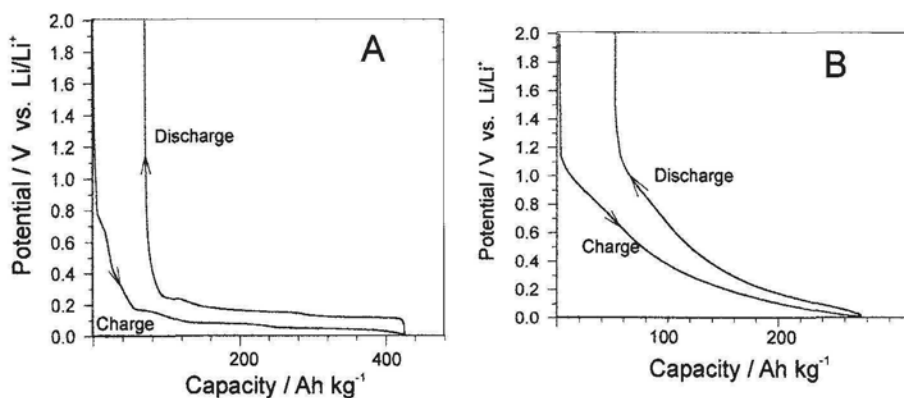


Figure 5.37. Typical 1<sup>st</sup> cycle characteristics of graphite (A) and soft carbon (coke) (B). (From Ref. 56)

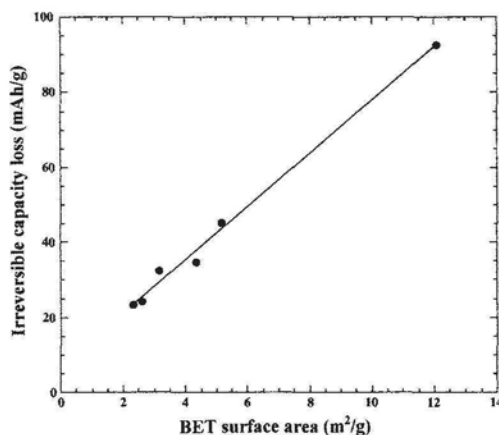


Figure 5.38. Dependence of the 1<sup>st</sup>-cycle irreversible capacity on the surface area of natural graphite in LiClO<sub>4</sub>-EC-DMC (1:1). (The acronym BET is derived from the inventors of the method for measuring the surface area, Brunauer, Emmet and Teller). (From Ref. 57)

and the overall capacity is lower with respect to graphite, all these factors contributing to a lower energy. On the other hand, it is noteworthy that, when graphite is used, some solvents tend to intercalate in its layers causing exfoliation and rapid deterioration. Propylene carbonate has such an effect and has to be avoided in connection with graphite or graphitic carbons, while it can be used with less crystalline carbons.

From the 2<sup>nd</sup> cycle on, the charge/discharge efficiency tends to the unity. In a practical cell, the situation is the one shown in Figure 5.39, where the

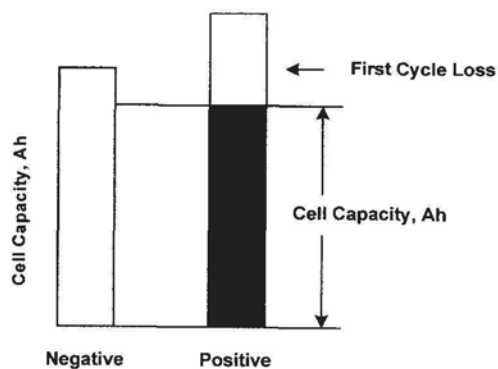


Figure 5.39. Relationship between the negative and positive electrode capacity in a Li-ion cell. (From Ref. 58)

positive is in excess to allow SEI formation, while the graphite capacity is not fully exploited [58]. This prevents reaching a voltage of 0 V on charge (see Figure 5.37), which would cause the unwanted Li plating on C. Normally, the capacity of the carbon electrode exceeds that of the positive electrode by 10% after the first cycle.

### 5.7.2. Positive Electrodes

As anticipated, almost all commercial Li-ion batteries for electronics use  $\text{LiCoO}_2$  as a cathode. This is a layered material whose structure is represented in Figure 5.40. It can be described as a hexagonal structure in which the  $\text{CoO}_2$  slabs are separated by Li layers.  $\text{Li}^+$  can entirely be removed from this structure, thus leading to  $\text{CoO}_2$ . This would correspond to a specific capacity of 273 mAh/g. However,  $\text{Li}^+$  re-intercalation after such a deep de-intercalation is not practical, although feasible in principle [54]. Therefore, a maximum delithiation of about 60% is allowed, this corresponding to a capacity of  $\sim 160$  mAh/g.  $\text{LiCoO}_2$  is characterized by a high potential vs. the graphite electrode. Indeed,

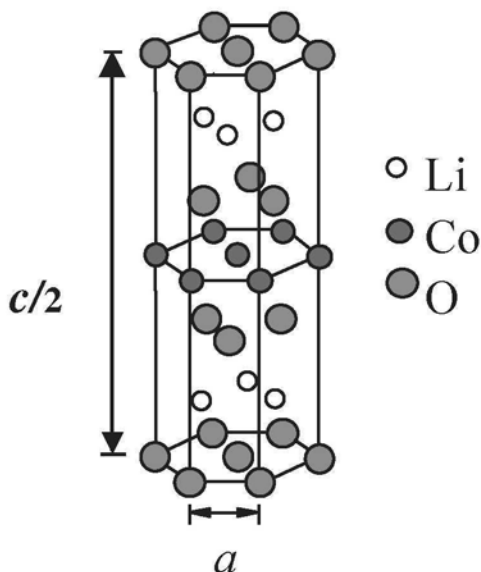


Figure 5.40. Crystal structure of  $\text{LiCoO}_2$  showing the alternating layers of Li, Co and O. (From Ref. 59)

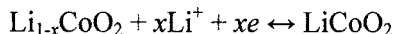


discharge curves at moderate rates occur at voltages from  $\sim 4$  V to  $\sim 3.5$  V. These values, coupled with the fairly high capacity mentioned above, grant high energy values.

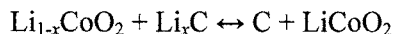
Other features of  $\text{LiCoO}_2$  include the following: high charge/discharge efficiency in the 1<sup>st</sup> cycle, thermal and chemical stability, and long-term cyclability. The main disadvantage of this material is represented by its high cost. However, it can be stressed once again that the cost has to be calculated on the basis of the energy delivered (Wh). Two prospective cathodes for Li-ion cells are  $\text{LiMn}_2\text{O}_4$  and  $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$  (see later for some more details on these materials). The price of  $\text{LiCoO}_2$  is about twice that of  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  and about four times that of  $\text{LiMn}_2\text{O}_4$ . However, if the price is related to the energy, a  $\text{LiCoO}_2$ -based battery is only 30% more expensive than batteries with cathodes containing Ni or Mn. This can be tolerated in the small cells used in portable electronics, where the cost of the active material has a lower impact with respect to the total cost.

The preparation of this material is rather simple. An example is given by the Sony method [60]:  $\text{Co}_3\text{O}_4$  and  $\text{Li}_2\text{CO}_3$  (in slight excess) are heated under air flow at  $950^\circ\text{C}$ . Particles of about  $20\text{ }\mu\text{m}$  are obtained with the use of polyvinyl alcohol added to the mixture. This particle size is optimum for a good electrochemical performance, while minimizing reactions with the electrolyte and, in general, safety problems.

The  $\text{Li}^+$  intercalation/de-intercalation reaction of  $\text{LiCoO}_2$  can be described as:



Combining this reaction with that of graphite (page 121), one obtains the overall reversible process in a C/ $\text{LiCoO}_2$  cell:



In this case, the couple  $\text{C} + \text{LiCoO}_2$  represents a cell in the fully discharged state.

In conclusion of this subsection, it has to be stressed that batteries with  $\text{LiCoO}_2$  have now reached energy densities in excess of  $150\text{ Wh/kg}$  and  $400\text{ Wh/L}$ , cycle lives in excess of 1000 cycles and low self-discharges ( $<3\%$ /month). The industrial processes are well established and high levels of mass production of portable batteries have been achieved through huge investments. On this basis, the substitution of  $\text{LiCoO}_2$  with another cathode could only be considered if the alternative were highly attractive in terms of performance and price.

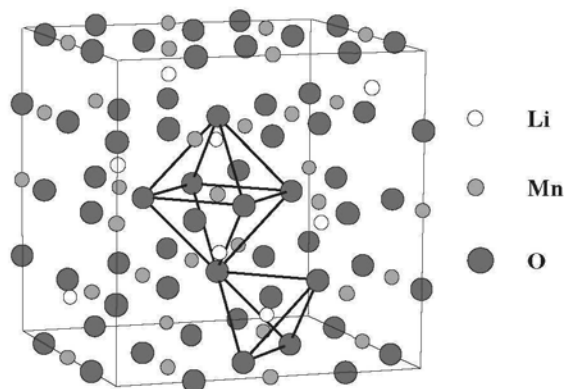


Figure 5.41. Crystal structure of spinel  $\text{LiMn}_2\text{O}_4$ . (From Ref. 59)

In some commercially available batteries used, at least for the moment, in specific niches, the positive electrode is  $\text{LiMn}_2\text{O}_4$ . Its spinel-type structure is depicted in Figure 5.41. At variance with  $\text{LiCoO}_2$ , this is a tridimensional structure that can accept  $\text{Li}^+$  in its tunnels. In comparison with  $\text{LiCoO}_2$ , advantages of this material are: flatter and higher voltage profile, higher thermal stability, lower cost. Negative points are: lower charge/discharge efficiency in the 1<sup>st</sup> cycle, lower discharge capacity (110–120 mAh/g vs. ~150 mAh/g), lower cycling stability especially at elevated temperatures.

Apart from the spinel  $\text{LiMn}_2\text{O}_4$ , of prospective use in large batteries (e.g. those for electric traction), few other materials can be considered promising.

By partially substituting Ni for Co in  $\text{LiCoO}_2$ , one obtains  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ . Some reports in the last years have indicated the possibility of using this material in practical batteries, as it has a couple of advantages over pure  $\text{LiCoO}_2$ : lower cost and higher capacity. On the other hand, it is less thermally stable and not long cyclable. Of greater interest seems to be its aluminium-doped derivative,  $\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$ . It contains more than 75% of the relatively cheap Ni, can be prepared on a large scale and affords high and stable capacities [54].  $\text{LiFePO}_4$  also appears of interest for its high theoretical capacity (170 mAh/g), flat voltage at ~3.4 V, low cost and safety. However, concern has been recently raised on its low volumetric energy density, which may seriously affect the possibility of a practical application [61]. Close attention are also receiving layered Mn-containing materials, such as  $\text{Li}[\text{Li}_{0.2}\text{Cr}_{0.4}\text{Mn}_{0.4}]\text{O}_2$  and  $\text{Li}[\text{Ni}_x\text{Li}_{(1/3-2x/3)}\text{Mn}_{(2/3-x/3)}]\text{O}_2$  [54].

### 5.7.3. Liquid Electrolytes

The pre-requisites of organic liquid electrolytes to be used in Li-ion batteries are essentially those mentioned for primary Li cells (page 57). Two of them are of particular importance, due to the specific nature of the electrode materials in Li-ion systems: a) The electrolyte has to grant a stable and efficient SEI on graphite, capable of limiting self-discharge (e.g.  $\text{Li}^+$  de-intercalation) and of allowing fast reversible  $\text{Li}^+$  transport; b) The electrochemical stability (window) of the electrolyte has to range from 0 V to at least 4.3 V vs. a  $\text{Li}/\text{Li}^+$  reference electrode. Indeed, at full charge, the graphite electrode has a voltage approaching 0 V vs.  $\text{Li}/\text{Li}^+$ , while  $\text{LiCoO}_2$  approaches 4.2 V for a charge state corresponding to 150-160 mAh/g.

Electrolytes commonly used in Li-ion batteries are based on  $\text{LiPF}_6$  as a salt and a binary solvent mixture, EC-DMC or EC-DEC. Their room temperature specific conductivities are in the range 7-10 mS/cm for 1 molar concentration of the salt, while at the upper usable limit of 60°C the conductivities are in the range 14-20 mS/cm. Solutions of  $\text{LiPF}_6$  in EC-DMC and EC-DEC are either solid or liquid with a very low conductivity at -40°C. For instance, a 1 M  $\text{LiPF}_6$  solution in EC-DEC has a conductivity of only 0.7 mS/cm at -40°C. This low conductivity has been taken for quite some time as the main responsible of the poor performance of Li-ion cells at low temperatures. It has been reported that the capacity at -40°C drops to 12% of that at room temperature. On this basis, a number of ternary or quaternary solvent mixtures with better low-temperature conductivities have been proposed. A good electrolyte is the one formed by 1 M  $\text{LiPF}_6$  in EC-DEC-DMC, whose stability and performance at room temperature are also good [63].

However, it has been found out that the graphite electrode plays a very important role in this poor low-temperature performance [62]. Indeed, in these conditions,  $\text{Li}^+$  diffusivity within the graphene layers is slow and the graphite capacity is limited. Therefore, an alternative to graphite has to be found if a satisfactory performance at temperatures below -30°C is sought.

At the other extreme, temperatures above 60°C are problematic for Li-ion cells operation [64]. While at the positive electrode parasitic reactions with the electrolyte are fastened, the SEI on the C surface becomes unstable. It can reform but is found to cause irreversible losses in the cell. Additives to improve the SEI are vinylene carbonate, used by SAFT and Sanyo, and methyl cinnamate, used by NEC.

One of the greatest concerns with liquid electrolytes is their flammability, which becomes a source of risk in case of cell venting. Additives that may lower the flammability (fire retardants) include trimethyl and triethyl phosphate, and other P-containing organic compounds [64].

Other additives may be added to the electrolyte to avoid problems created by overcharges. A current interrupting device (CID) may be activated if during overcharge a gas is generated (see, for instance, Figure 7.2). Additives of this type include: cyclohexylbenzene (Asahi), biphenyl (NEC) and pyrocarbonate (Sony) [64].

Liquid electrolytes need to be supported by microporous separators. All Li-ion cells use polyolefin films whose characteristics include:

- Chemical stability toward electrodes and electrolytes
- Mechanical stability
- Thickness of 10-30  $\mu\text{m}$
- Pore size less than 1  $\mu\text{m}$
- Easy electrolyte absorption (wettability)

Polyethylene and propylene are most widely used. They can also act as a thermal fuse. Indeed, the former melts at 135°C and the latter at 165°C. If the cell temperature reaches these values, melting of the polyolefin films shuts their pores and no current flow is further allowed. Bi- or tri-laminates of these separators can also be used.

#### 5.7.4. Cell Construction and Performance (with Liquid Electrolytes)

*Cell construction.* Commercial Li-ion cells are mainly available in cylindrical or prismatic form factors, but a limited production of button cells has also been started. In cylindrical and prismatic cells, the electrodes and separators are wound together, as shown in Figures 1.7(a,c) and 5.42.

The negative electrode is supported on a thin Cu foil (10-20  $\mu\text{m}$ ) and has a total thickness of  $\sim 200 \mu\text{m}$ . The positive electrode is supported on a thin Al foil (10-25  $\mu\text{m}$ ) and has a total thickness of  $\sim 180 \mu\text{m}$ . The separator (see previous sub-section) is inserted in between and the three ribbons are wound around a cylindrical or flat mandrel for cylindrical or prismatic cells, respectively. The case is normally the positive electrode and is made of stainless steel. However, the last generation of prismatic cells uses an Al case to take advantage of its lower weight. The cell cap often contains a PTC device (see also Chapter 7) and a safety vent (Figures 5.42 and 7.2).

*Capacity vs. rate and temperature.* Cylindrical cells have capacities ranging from  $\sim 0.7$  to  $\sim 2.5$  Ah. The most popular size, 18650 (diameter: 18 mm, height: 65 mm), has had an impressive capacity gain since its introduction in 1991. From the initial value of 1 Ah, the capacity has reached the present value of 2.4 Ah, thanks to active materials and cell improvements. These cells have now good rate and temperature characteristics (Figures 5.43 and 5.44). The wound and thin electrode design allows high rate capability in spite of

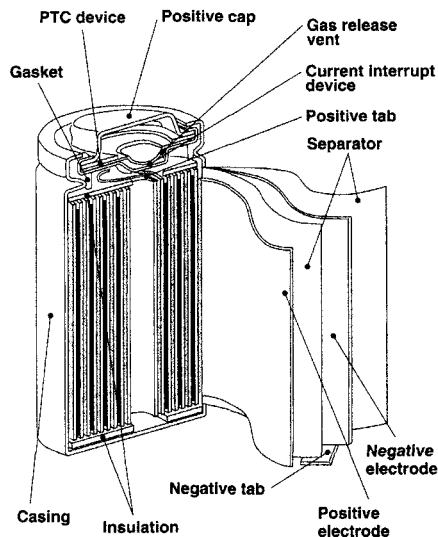


Figure 5.42. Construction of a Li-ion cylindrical cell. Note the PTC device and the vent. (Courtesy of Sanyo)

the lower conductivities of organic electrolytes with respect to the aqueous ones. A ten-fold increase in the discharge current causes a limited capacity decrease (Figure 5.43a), and a similar increase in the constant-power discharge corresponds to a limited energy decrease (Figure 5.43b).

The discharge characteristics at various temperatures are shown in Figure 5.44. The capacity loss is limited even at  $-20^{\circ}\text{C}$ , but at this temperature the voltage drop and the related energy penalty are remarkable.

The rate capability of a prismatic cell is shown in Figure 5.45. It may be appreciated that the capacity losses at rates above 1C are larger than those found in cylindrical cells. This is to be related to the different cell geometry. In a cylindrical cell, no voids are left and the tight configuration does not allow any deformation. In a prismatic cell, the wound electrodes leave some free space and, furthermore, the light Al casing may be undergo some deformation. The low temperature performance of the prismatic cells is also less satisfactory.

*The charging technique.* Li-ion batteries are normally charged with a double-step process: in the first, a constant current (CC) is applied until the voltage reaches a prefixed value (usually 4.2 V per cell); in the second, the cell is maintained at the constant voltage (CV) reached at the end of the previous step, while the current decays. The charge is terminated when the current reaches values of  $C/10$ - $C/30$ . A correct charge is done under control, and the end of charge is signalled by both the current value and the total time: a too

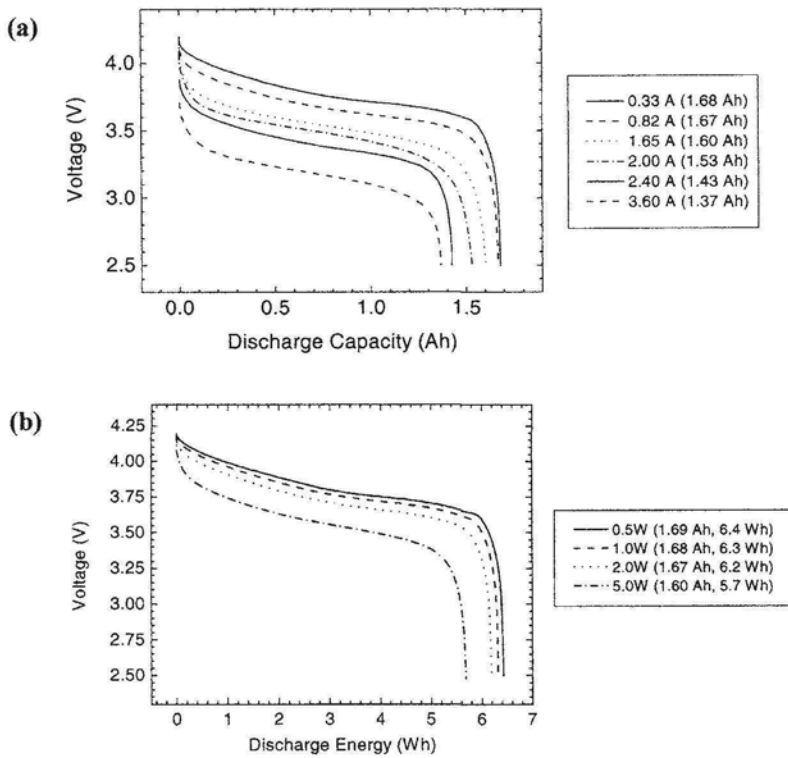


Figure 5.43. Discharge rate characteristics of a cylindrical Li-ion cell (18650): (a) constant current; (b) constant power. (From Ref. 65)

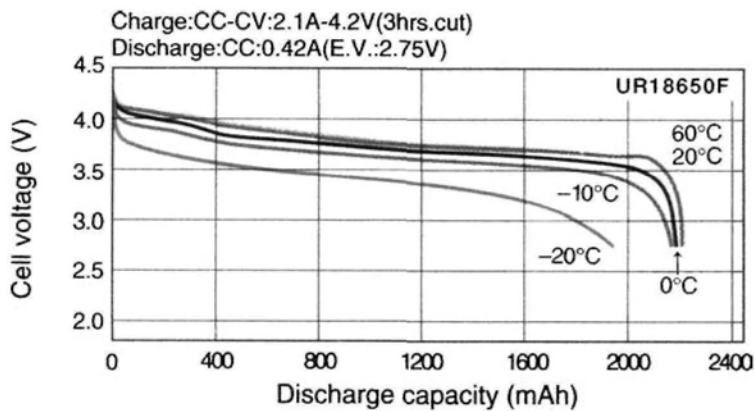


Figure 5.44. Discharge characteristics as a function of temperature for a cylindrical Li-ion cell. (Courtesy of Sanyo)

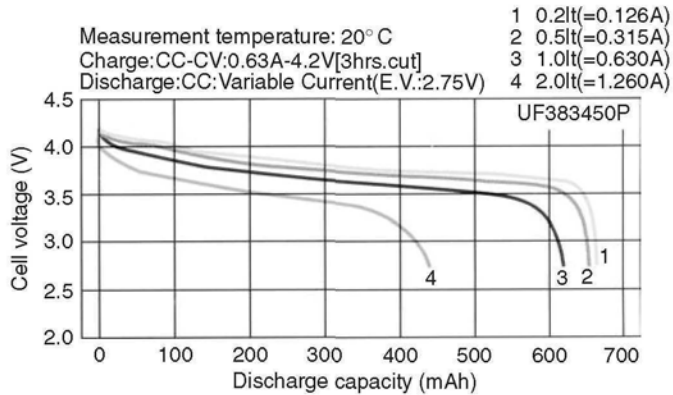


Figure 5.45. Rate capability of a prismatic Li-ion cell (630 mAh). (Courtesy of Sanyo)

long charge reveals some problems, so it will be automatically stopped. In Figure 5.46, the trend of current, voltage and capacity is plotted as a function of time. The CC step has a current limit to avoid excessive cell heating. Conversely, if the initial cell voltage is below 2.5 V, the charge current should be low, say 0.1C. If the initial cell temperature is too high, the charge cannot start until cooling. The charge has to be done in a precise temperature range, e.g. 0-45°C.

The total charge time is 2-3 hours and typical charge currents are 0.7-1.0C. A higher current to speed the charge is useless: the top voltage will be reached sooner but the CV step will last longer. However, the recently introduced pulse charging technique can short the charging time. According to

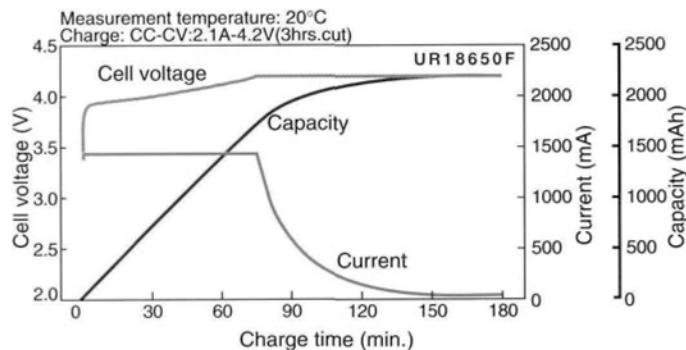


Figure 5.46. CC-CV charging of a Li-ion cell. (Courtesy of Sanyo)

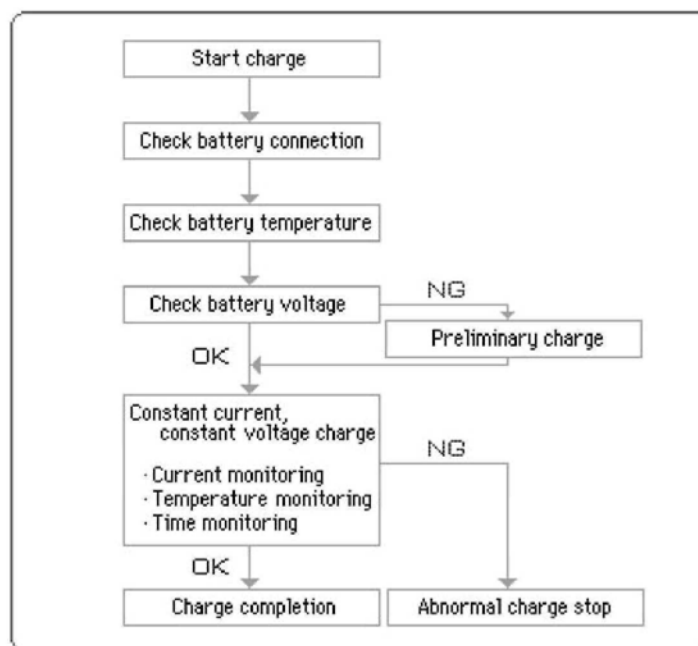
Sanyo, a full charge can be reached in 90 minutes (see Chapter 7 for more details). Trickle charge is to be avoided: more  $\text{Li}^+$  can be withdrawn from  $\text{LiCoO}_2$ , exposing it to the risk of loss of reversibility, and excess  $\text{Li}^+$  could be plated on C.

A flowchart showing the basic controls during a Li-ion charge is shown in Table 5.10.

**Charge retention.** Last-generation Li-ion cells lose a minor fraction of their capacity upon room-temperature storage. This is shown in Figure 5.47 for a cylindrical cell stored in the fully charged state at 20°C for six months. The monthly capacity loss is 1.7%, a remarkable result in comparison with the losses of other rechargeable systems, especially the Ni-Cd and Ni-MH cells (see also Table 5.1).

A complete recharge after storage, followed by a complete discharge shows that a fraction of the initial capacity is irreversibly lost. In Figure 5.47, the permanent loss corresponds to 3%. As any other chemistry, a Li-ion cell is rather sensitive to a temperature increase. Indeed, six-month storage at 40°C causes a total capacity loss of 40%, while at 60°C the loss is 80%. The

Table 5.10. Example of charge control flowchart for constant current and constant voltage battery chargers. (Courtesy of Maxell)





corresponding permanent loss also increases with temperature. This evidence clearly suggests not storing these cells for a long time, especially in a hot place.

**Cycling characteristics.** Li-ion cells have long cycle lives. They can sustain hundreds of deep cycles at high rates and in a relatively wide temperature range. Cycling of a commercial cell is shown in Figure 5.48. At room temperature and at the C rate, the cell can deliver 500 cycles (at 100% DOD) to 80% initial capacity.

This behaviour is satisfactory but a steady decrease (capacity fade) can be observed with cycle number. This is more evident as the temperature is increased, although the C/LiCoO<sub>2</sub> system can limit losses much better than the C/LiMn<sub>2</sub>O<sub>4</sub> system. Investigations on the causes of the capacity fade for C/LiCoO<sub>2</sub> cells have shown that the main responsible for this is the cathode. Indeed, its interfacial resistance grows remarkably with cycling, as ascertained with impedance tests [67], because of oxidation phenomena.

The rapid capacity fade of the C/LiMn<sub>2</sub>O<sub>4</sub> system has been the subject of numerous studies. In this case, too, the positive electrode was responsible for the fade. However, more recent commercial cells based on this system have proven able to limit capacity losses also at relatively high temperature (see, *e.g.*, Ref. [54] and Sanyo's catalogs).

Other factors determining capacity loss upon cycling are DOD, discharge rate and voltage limit on charge. Cells brought to a voltage charge of 4.2 V provide an initially higher capacity *vs.* cells charged to 4.1 V, but the rate of their capacity fade is faster. Similarly, cells not completely discharged (DOD<100%) can live much longer. A commercial cell providing 400 cycles at

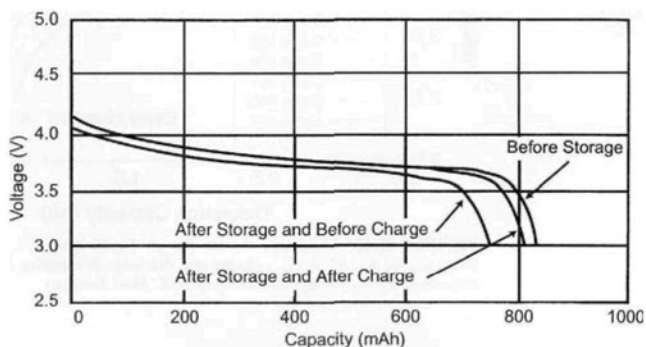


Figure 5.47. Storage characteristics of a cylindrical Li-ion cell. Six months at 20°C. (From Ref. 66)

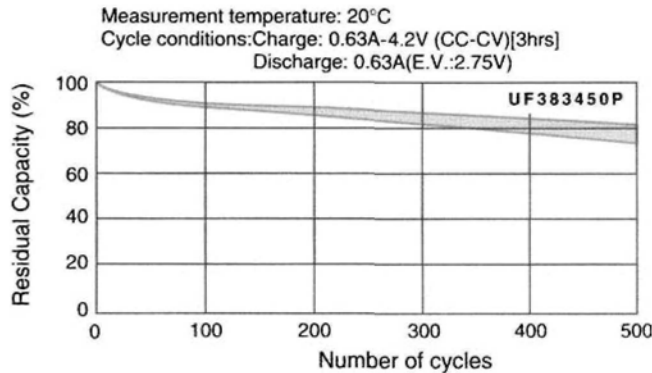


Figure 5.48. Cycling of a prismatic Li-ion battery (630 mAh). (Courtesy of Sanyo)

100% DOD has reached 10000 cycles at 25% DOD. An experimental cell cycled for 1000 cycles at 100% DOD has lost 70% of its capacity at the C/2 rate, and 40% at the C/25 rate. However, if the DOD is kept at 70%, no capacity loss was observed for 1000 cycles [68]. This can be of some help for the end user. Indeed, the parameters fixed by the manufacturer cannot be changed, but one can take advantage of the state-of-charge indicator in the device's display. Whenever the display shows that the battery is reaching about  $\frac{1}{4}$  of the charge state or, anyway, the signal of low-battery appears, the battery should be soon recharged.

A comparison of cylindrical and prismatic batteries by the same manufacturer (Sanyo) shows that the latter can cycle longer in the same conditions (*e.g.* 1C discharge rate). Prismatic cells now have a light case, which can be of two types: the "hard" case (see Figure 1.7a) and the "soft" case (the latter is a thin plasticized Al foil, see Figure 1.8; cells with this case are also called pouch cells). Both cells show an expansion at the end of a charge or upon extended cycling [69]. This phenomenon depends on cell manufacture and cycling conditions. It does not impair cell cyclability, but has to be taken into account especially when several cells are stacked and connected.

Table 5.11 presents the relevant data of recent commercial cells. The largely used 18650 cell, with a rated capacity of 2.1 Ah, has a specific energy exceeding 160 Wh/kg and an energy density well above 400 Wh/L. Prismatic cells have higher specific energies thanks to the use of the lightweight Al case (compare cells of the same capacity, *e.g.* 720 and 1700 Ah).

The data for cell packs are obviously lower than those of Table 5.11, as external case, electronics and other internal inactive parts have to be included.

Table 5.11. Examples of cylindrical and prismatic Li-ion cells with liquid electrolyte. (Courtesy of Sanyo)

Cylindrical Cells						
Capacity (mAh)	Diameter (mm)	Height (mm)	Weight (g)	Spec. Energy <sup>1</sup> (Wh/kg)	Energy Dens. <sup>1</sup> (Wh/L)	
720	13.9	49.2	19.5	136	356	
940	13.9	64.7	26	134	355	
1500	18.1	49.3	35	158	438	
1700	17.6	64.7	41.5	151	400	
2100	18.1	64.8	46.5	167	466	

Prismatic Cells						
Capacity (mAh)	Thickness (mm)	Width (mm)	Height (mm)	Weight (g)	Spec. Energy <sup>1</sup> (Wh/kg)	Energy Dens. <sup>1</sup> (Wh/L)
200	6.0	19.1	27.8	7	106	232
420	5.8	19.1	47.8	11.5	135	293
720	4.3	33.8	49.8	16.7	159	367
900	10.3	22.5	47.8	24	139	333
1700	10.5	33.8	48.8	39.5	159	363

Discharge at 0.2 C; charge CC-CV at 1C to 4.2 V, 2.5 h. Nominal voltage: 3.7 V

<sup>1</sup>Values calculated by the author with the weight and volume data of the table

The decrease is a function of the cells enclosed in the pack: a 1-cell pack has an energy density of 200-230 Wh/L but a 6-cell pack has 300-330 Wh/L.

*Special Li-ion cells.* Apart from the C/LiMn<sub>2</sub>O<sub>4</sub> cell, few other commercial Li-ion cells are not based on the C/LiCoO<sub>2</sub> couple. A button cell for memory backup applications is based on a positive electrode indicated as Li<sub>x</sub>Ti<sub>y</sub>O<sub>4</sub> [5]. Quite possibly, this is Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, a material giving with graphite a nominal voltage of 1.5 V. This small cell, with capacity of few mAh, is reported to be capable of 500 cycles and quick charges.

Another 1.5 V button cell for memory backup (paggers and timers) or watches is based on a couple not using graphite. The negative electrode is just Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> mentioned above. The positive electrode is not disclosed, but is referred to as Li-Mn oxide [24,70]. This cell too can sustain 500 cycles and, because of the specific nature of its electrodes, can stand overcharge and overdischarge.

The use of a negative electrode not based on carbon is now receiving renewed attention. Several inorganic materials, including oxides, silicides, phosphides and nitrides are being investigated with the aim of finding negatives with higher capacities and lower initial irreversible capacity [53].

### 5.7.5. Li-Ion Batteries with Polymeric Electrolytes

The use of polymeric electrolytes for Li and Li-ion batteries had several false starts until 1999, when finally the first batteries were commercialized. Cells with polymeric electrolytes can offer some advantages over the conventional ones, *e.g.* no leakage, flexibility and very thin form factors. Attempts to use “dry”, solvent-free polymeric electrolytes in cells working at ambient or sub-ambient temperature have so far failed, as their conductivity are too low. On the other hand, the use of the so-called gel polymer electrolytes has resulted in commercial products with performance characteristics comparable with those of liquid-electrolyte Li-ion cells.

*Polymer electrolyte and cell construction.* A gel polymer electrolyte (GPE) is formed by immobilizing a liquid electrolyte in a polymeric matrix. Various polymers have been proposed for this purpose, *e.g.* poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVDF), poly(ethylene oxide) (PEO) and poly(acrylonitrile) (PAN). There are two approaches to make a GPE: in the first, the liquid electrolyte is added to the polymer matrix, which immobilizes it within its pores; in the second, polymer and electrolyte form a homogeneous phase. This latter condition may be obtained either by mixing polymer powder and electrolyte in a common solvent (which is then evaporated), or by adding to the electrolyte a polymer precursor and forming the polymer *in-situ*.

Whatever the approach, desirable features of a gel electrolyte are:

- Solvent confinement within the polymer structure, *e.g.* no free solvent available that may cause leakage
- Low vapor pressure of the solvents
- High conductivity at room temperature and below
- Good adhesion to the electrodes

The *in-situ* polymerization technique is exploited by Sanyo in their commercial Li-ion polymer cells. The cell is formed according to the usual technique for liquid electrolytes and, in the final step, a polymer precursor is added and heating is applied to polymerize [71]. The electrolyte is  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$  in EC-DEC and the polymer is cross-linked PEO. This type of gel electrolyte is shown in Figure 5.49.

In Sony's approach, the gel electrolyte is formed separately. They have chosen a copolymer of PVDF and poly(hexafluoropropylene) (PHFP) and an electrolyte formed by  $\text{LiPF}_6$  in PC-EC [71]. The PHFP content in the copolymer is kept low (3-7.5% by weight) to maintain the mechanical strength typical of crystalline PVDF. PHFP grants good electrolyte absorption. The presence of PC in a cell with a graphite negative electrode may be surprising as PC is decomposed while graphite is exfoliated. In Sony's cells the graphite is coated

with amorphous carbon, so to avoid decomposition. Indeed, the irreversible capacity of the 1<sup>st</sup> charge is lower than 10%. The conductivity of this gel electrolyte, 9 mS/cm at 25°C, is comparable to those of liquid electrolytes and represents a remarkable improvement over 1<sup>st</sup>-generation electrolytes, as shown in Figure 5.50. This was made possible by optimization of: salt concentration, PC/EC ratio, VDF/HPF ratio and molecular weight of the copolymer [71]. Sony's electrolyte can be shaped into self-standing membranes. Electrodes, electrolyte membrane and a 10- $\mu$ m separator (to prevent mechanical short circuits) are wound together around a flat mandrel and this assembly is inserted into a bag made of laminated (on both sides) Al foil. The bag is tightly closed to avoid moisture infiltration.

Li-ion cells with polymer electrolytes are 3-4 mm thin, but can be as thin as 2 mm. An external/internal view is shown in Figure 5.51. All cells use graphite as a negative electrode. As far as the positive is concerned, LiCoO<sub>2</sub> maintains its prevalent position, but LiMn<sub>2</sub>O<sub>4</sub> is gaining importance and is used by some manufacturers, *e.g.* Sanyo, NEC, Valence and Ultralife (see also Appendix G).

*Cell performance.* The rate capability of a Li-ion polymer cell is shown in Figure 5.52. This cell, with a composite LiMn<sub>2</sub>O<sub>4</sub>/LiCoO<sub>2</sub> positive electrode, can sustain high rates. A similar prismatic cell with a liquid electrolyte and LiCoO<sub>2</sub> as a positive does not show a comparable performance (Figure 5.45). The compact structure of the polymeric cell, with excellent adhesion of the

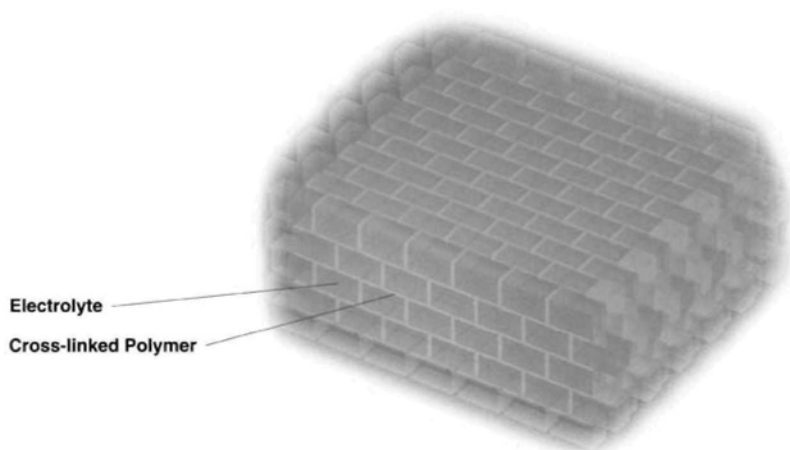


Figure 5.49. Model of a gel-type polymer electrolyte. The electrolyte is contained within the tridimensional network of the polymer. (Courtesy of Sanyo)

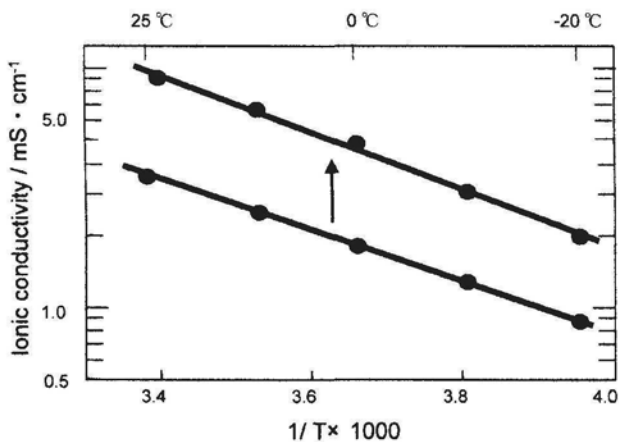


Figure 5.50. Conductivities of first-generation (*lower line*) and second-generation (*upper line*) electrolytes used in Sony's Li-ion polymer cells. (From Ref. 71)

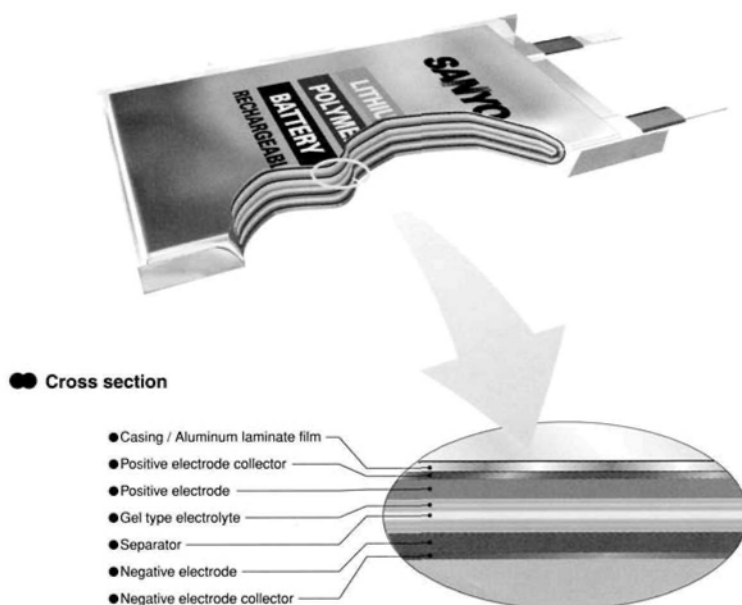


Figure 5.51. Li-ion cell in a laminated Al bag. (Courtesy of Sanyo)

electrode/electrolyte stack, is thought to be the reason for this performance.

These cells also perform well in a wide temperature range. At -20°C and

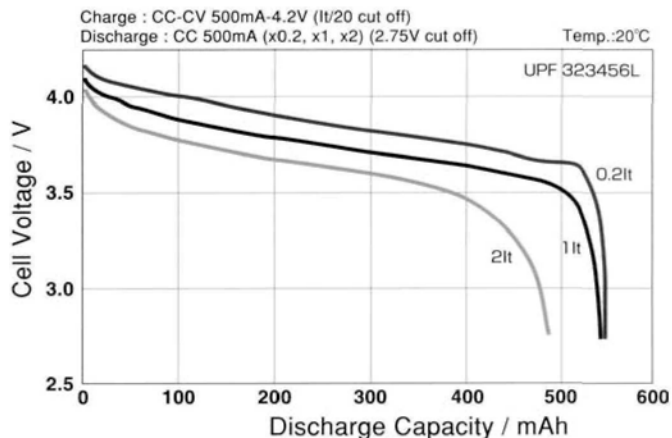


Figure 5.52. Rate capability of a polymeric Li-ion cell (500 mAh).  $\text{LiMn}_2\text{O}_4/\text{LiCoO}_2$  composite positive electrode. (Courtesy of Sanyo)

at  $C/2$  rate, a cell with a good electrolyte can retain 60% of its room temperature capacity, as shown in Figure 5.53.

As far as cyclability is concerned, last-generation cells seem able to outperform liquid-electrolyte cells. More than 1000 cycles at 100% DOD are

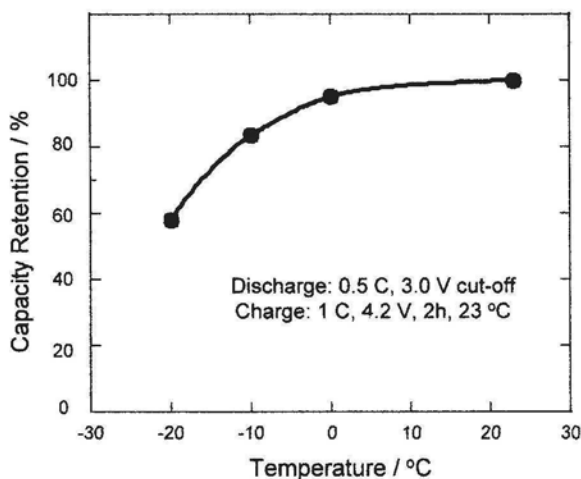


Figure 5.53. Capacity retention of a polymeric Li-ion cell ( $\text{LiCoO}_2$ ) vs. temperature. (From Ref. 71)

achievable at the 1C rate (Figure 5.54), and the capacity at the 1000<sup>th</sup> cycle is still 85% of the initial one.

Li-ion cells are now largely used to power cellular phones, where the ability to sustain high-current pulses is needed. One of these pulse regimes can be found in the GSM phones now used worldwide. Typical load characteristics of a GSM phone are presented in Figure 5.55 (left). A current corresponding to a rate usually above 2C is drawn for 0.5-0.6 msec when transmitting at maximum power, while a base current of 150-200 mA has to be maintained for 4-5 msec.

Li-ion polymer cells have been tested under the GSM regime and the results are shown in Figure 5.55 (right). The performance is good at the temperature of -20°C too, where 40% of the room-temperature capacity is maintained. This regime can be sustained for several cycles. As shown in Figure 5.56, 85% of the initial capacity is still recoverable after 660 cycles at the pulse current of 2.7 A (2.6C rate).

These Li-ion cells can be made in a variety of sizes to suit the OEMs requests. Standard sizes include the ones listed in Table 5.12 (Sanyo). The first two batteries in this table contain a positive based on  $\text{LiMn}_2\text{O}_4$ , but also  $\text{LiCoO}_2$  is included so to limit cycle life deterioration of the former and gas generation [72]. Li-ion cells with this composite cathode are said to be able to sustain overcharge, and can be built without a protection circuit. Some commercial cells use a passive safety element, *e.g.* the so-called polymeric positive temperature coefficient (PPTC) device. This element is described in detail in Chapter 7.

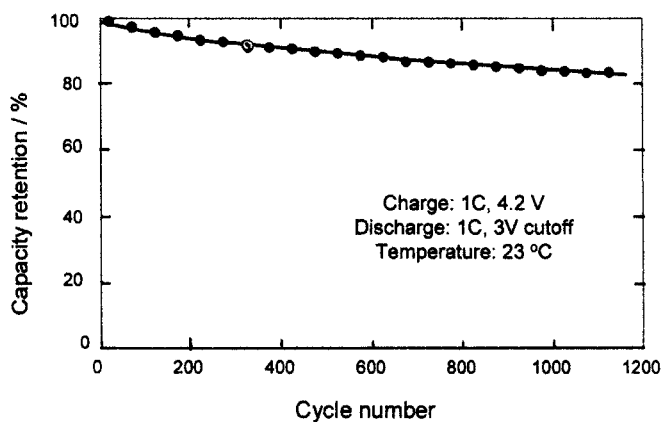


Figure 5.54. Cycle characteristics of a Li-ion polymer cell ( $\text{LiCoO}_2$ ) at the 1C rate. (From Ref. 71)



Sony's Li-ion battery mentioned above, with a  $\text{LiCoO}_2$  positive, has a reported specific energy of 190 Wh/kg and an energy density of 375 Wh/L.

### 5.7.6. Applications

Li-ion batteries are now the batteries of choice in these consumer applications: PDAs, digital still cameras (DSC), camcorders, cell phones and notebooks. Cylindrical batteries, with special reference to the 18650 model, are especially used, as packs, in laptop computers and camcorders. The former devices draw powers in the range 10–40 W, with a maximum current of  $\sim 1$  A. As shown in Figure 5.43, a cylindrical cell can stand these drains. In camcorders, powers are in the range 2.5–3 W (maximum current  $\sim 0.5$  A) [74]. Pouch cells (soft package) are particularly used in cellular phones and palmtops. The tough GSM regime has been mentioned above, while the current in a palmtop is usually 0.1 A but can rise to 0.5 A if the display is backlit [73].

The evolution of Li-ion batteries has been remarkable in these years. Today, their maximum specific energies are approaching 200 Wh/kg and their energy densities 520 Wh/L (see also Chapter 10). However, it seems that the limits are very near: a calculation has set to 550 Wh/L the maximum value of energy density.

The number of prismatic cells is rapidly growing at the expenses of the cylindrical ones. This trend is being driven by cellular phones, which are now mostly based on a single flat cell. Polymer cells are exponentially growing

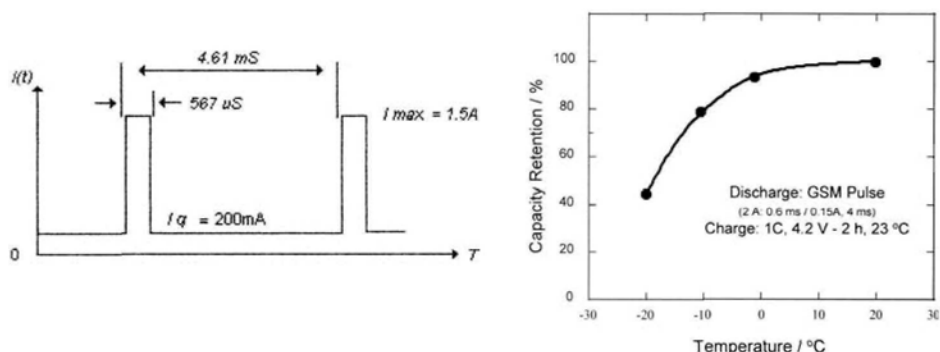


Figure 5.55. Typical GSM waveform (left) and behavior of a 760-mAh polymeric cell ( $\text{LiCoO}_2$ ) at the regime specified in the figure and different temperatures (right, from Ref. 71)

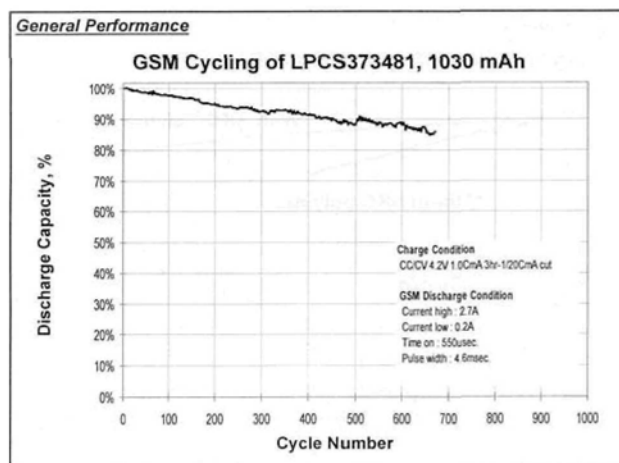


Figure 5.56. Cycling characteristics of a 1030-mAh Li-ion polymer cell ( $\text{LiCoO}_2$ ) at the GSM regime (2.7 A/0.2 A). (From Ref. 73)

especially in cell phones and PDAs. More details on the applications and market shares of these batteries will be given in Chapter 10. It can be anticipated that they will be prevalent in the market at least for the next 3-5 years.

### 5.7.7. Care of Li-Ion Batteries

Li-ion batteries need no maintenance but care must be exercised to prolong their useful life. First, it has to be stressed that these batteries have a pronounced tendency to age even if not in use. Aging is a consequence of parasitic reactions, the most notable being that involving electrolyte and

Table 5.12. Examples of Li-ion polymer batteries. (Courtesy of Sanyo)

Capacity (mAh)	Thickness (mm)	Width (mm)	Height (mm)	Weight (g)	Spec. Energy (Wh/kg)	Energy Dens. (Wh/L)
500 <sup>1</sup>	3.2	34	56	13.3	139	299
640 <sup>1</sup>	3.9	34	56	14.5	163	319
620 <sup>2</sup>	3.7	34.7	61	15.4	149	293
940 <sup>2</sup>	3.6	34.5	80.5	21	166	348

1. Batteries with a positive electrode based on  $\text{LiMn}_2\text{O}_4$ ; 2. Batteries with a positive electrode based on  $\text{LiCoO}_2$ .

positive electrode. The electrolyte is consumed by this reaction that forms a layer on the positive – the battery tends to dry out with time and its resistance increases. Therefore, a Li-ion battery should not be long stored. Aging is faster at high temperatures, so the battery should be better stored in a cool place. This also suggests a way to prolong the life of a battery used in a notebook computer. The power requested by these computers is increasing and so does the heat they dissipate: inside a notebook the temperature is at least 45°C. When the computer is used at home or in the office, it should be powered by the AC current and the battery removed. A Li-ion battery can give 1000 cycles, but this number is severely reduced by cycling at 45°C or more. The tendency to aging suggests that a spare battery should be used only if really used, for instance by travellers who need their computer all day long.

The state-of-charge in storage is also very important. The battery should not be left on storage in the fully charged or fully discharged state. Many manufacturers recommend a 40%-50% SOC, as parasitic reactions are reduced at this intermediate discharge state.

As already stated, the battery's life can also be prolonged by avoiding 100% DOD discharges. Even if the state-of-charge indicators are often not very accurate (see Chapter 7), it is convenient to recharge the battery as soon as the indication of low remaining charge appears. Of course, a full recharge is to be avoided if the battery is going to be stored.

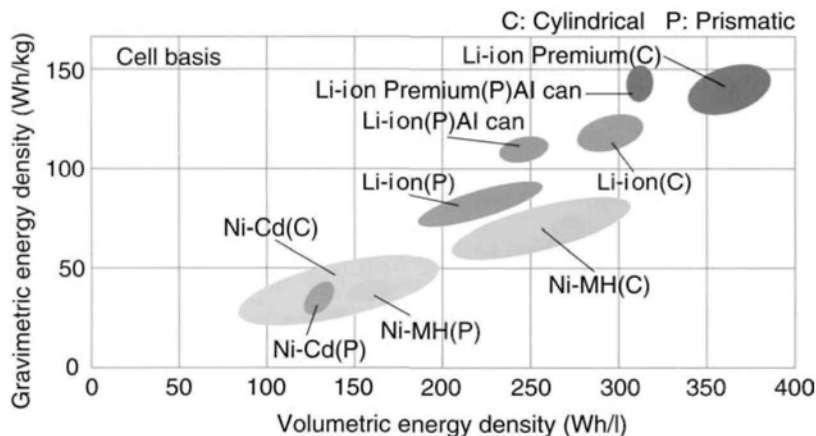


Figure 5.57. Comparison of the energy, on a cell basis, of Li-ion, Ni-Cd and Ni-MH batteries. Data updated to the end of 2003. (Courtesy of Sanyo)

Table 5.13. Comparison of the advantages and disadvantages of Ni-Cd, Ni-MH and Li-ion batteries.

	Ni-Cd	Ni-MH	Li-Ion
Advantages	<ul style="list-style-type: none"> <li>Fast charge also after prolonged storage</li> <li>Good rate capability</li> <li>Good low-temperature performance also on charge</li> <li>Long cycle life (1000-1500 cycles)</li> <li>No deterioration on storage</li> <li>Resistant to abuse</li> <li>Low cost</li> </ul>	<ul style="list-style-type: none"> <li>Higher energy than Ni-Cd</li> <li>Reduced memory effect</li> <li>No toxic components</li> <li>No transportation restrictions</li> <li>Cheaper than Li-ion and almost same price as Ni-Cd</li> <li>Fast charge possibility</li> </ul>	<ul style="list-style-type: none"> <li>High energy density</li> <li>No memory effect</li> <li>Low self-discharge</li> <li>Available in any size including very thin or peculiar shapes</li> <li>Long cycle life (more than 1000 cycles with LIP)</li> </ul>
Disadvantages	<ul style="list-style-type: none"> <li>Low energy values</li> <li>High self-discharge</li> <li>Memory effect</li> <li>Toxic components</li> </ul>	<ul style="list-style-type: none"> <li>Performance loss on deep cycling especially at high rates</li> <li>High self-discharge</li> <li>Charge requires control</li> <li>Best cycled at rates &lt; 0.5C</li> <li>Sensitive to storage at high temperatures</li> </ul>	<ul style="list-style-type: none"> <li>Aging on storage or use</li> <li>Protection circuit needed</li> <li>Limited rate capability at low temperatures</li> <li>Highest (but decreasing) cost</li> <li>Still some safety problems (flammable electrolytes)</li> </ul>

## **5.8. Comparison of Secondary Batteries for Portable Devices**

A comparison of Li-ion batteries with Ni-Cd and Ni-MH batteries is presented in Figure 5.57. It can be noted that some of the newest Li-ion batteries (Tables 5.11 and 5.12, and other data mentioned in the previous section) exceed the maximum energy values of the figure. Some advancements have also been achieved by recent cylindrical Ni-MH batteries: gravimetric energies of 90-95 Wh/kg and volumetric energies of 330-345 Wh/L are reported. On the other hand, the energies of Ni-Cd batteries seem steady.

NiMH batteries are loosing significant shares in cell phones and notebooks. They keep a fair but minor position in DSC, cordless phones and portable AV equipment. Ni-Cd batteries are the ones of choice for power tools, portable AV and cordless phones. The other applications are dominated by Li-ion batteries (see Chapter 10).

To complete the comparison of Ni-Cd, Ni-MH and Li-ion batteries, their main advantages and disadvantages are summarized in Table 5.13.

## Chapter 6

# BATTERIES FOR MEDICAL AND SPECIAL APPLICATIONS

## 6.1. Batteries for Cardiac Rhythm Management Devices

Basically, there are three types of devices treating cardiac diseases, *i.e.* pacemakers, cardioverter defibrillators and left ventricular assist devices. In addition, the total artificial heart also needs to be powered by batteries. Cardiac pacemakers are prescribed when the cardiac rhythm is too slow. The implanted devices detect the slow heart rate and send impulses to stimulate the muscle. The first implanted pacemakers required opening the chest cavity under general anaesthesia and had leads that were initially attached to the heart's surface. Subsequently, those reaching the heart through a vein replaced these leads. The life of the early devices, continuously pacing the heart at a fixed rate, was only 12-18 months. This was indeed the life of the Zn/HgO batteries used at that time [75]. Later, pacemakers *on demand* were introduced, which started to act only when a pre-set heart pace was not detected. Furthermore, in 1975, the Li/I<sub>2</sub> battery became available, which extended the battery life to 10 years. This primary Li battery was not dealt with in the section devoted to this class of batteries because of its special use. Therefore, its characteristics will be presented here (Sub-section 6.1.1).

A further remarkable progress was made with the use of titanium casing in place of the plastic materials previously used. With titanium (along with special filters) the device is shielded with respect to electromagnetic fields. A number of sources can emit such fields, *e.g.* power lines, radio frequencies (RF), cellular phones, personal communication devices, microwave ovens, *etc.* If these external signals have frequencies in the 10-100 Hz range, *i.e.* the same range of the sense amplifier of the pacemaker, there could be sensing/pacing inhibition or asynchronous pacing. High-power RF electromagnetic fields and high-voltage power transmission equipment also interfere with the pacemaker activity [76]. A further progress was made with the introduction of programmable pacemakers whose parameters could be set by external signals. This obviously eliminated the need of repeated surgical operations. In the early 1980s, pacemaker's leads were made available that could emit drugs to suppress inflammation of the heart wall [76]. Some years later, rate-responsive pacemakers were introduced: the body movements are detected and the pacemaker's rate is increased or decreased accordingly.

A pacemaker has two parts: the chamber and the lead(s). The pacemaker chamber contains a timing device for setting the pacing rate, a circuitry that detects electrical signals from the heart, and a battery. This last occupies half the total space. Some pacemakers have only one lead, and are called single-chamber; others have two leads and are called dual-chamber. The tip of the lead is placed in contact with the inner wall of the right atrium (upper cavity) or the right ventricle (lower cavity), while the other end of the lead is connected to the pacemaker chamber. Pacemakers can also be used to prevent episodes of abnormal rapid rhythms, such as atrial fibrillation, and are equipped with multiple leads implanted in the atrium. A pacemaker battery can usually last 7-10 years. When the battery is running low, the pacemaker will send a signal that can be detected by the doctor during a routine visit. A low battery still allows time for replacing.

Modern pacemakers act as micro-computers. For instance, they can store patient's data directly in the device memory and can monitor the heart activity so to change automatically the therapy delivered. This means that batteries with higher power capability than  $\text{Li/I}_2$  may be needed. Indeed, nowadays a number of options are available for the devices mentioned at the beginning of this section.

The implantable cardioverter defibrillator (ICD) is designed to detect and treat episodes of ventricular fibrillation, ventricular tachycardia, faster ventricular tachycardia and bradycardia. This device contains a high-voltage capacitor that provides a stimulus to the heart when the regular pace is lost due to ventricular problems. To power the ICD, a battery capable of delivering high current pulses is needed. An excellent power source is the Li/silver vanadium oxide (SVO) system presented in Sub-section 6.1.2. Also the  $\text{Li/CF}_x$  battery described in Sub-section 4.7.3 is well suitable and a battery containing both cathodes has been recently proposed [77].

The left ventricular assist device (LVAD) is used to help the important left ventricle to do its job of pumping blood to the body more effectively. It is intended for patients who are no longer responsive to medical therapy and are not candidates for heart transplants. This device requires rechargeable batteries and the Li-ions ones have proved suitable for delivering  $\sim 10$  W with a 12-V pack [78]. Current versions of this device are powered from external packs. In the last five years, clinical trials have been going on with a LVAD in which the batteries are also implanted. It operates with transcutaneous energy transmission to charge the batteries (not specifically mentioned – quite possibly Li-ion) [79].

The total artificial heart (TAH) is a mechanical pump that completely replaces the patient's heart. Several experimental TAHs have been implanted in patients recently. The design of this replacement heart contains two chambers,

each capable of pumping over 7 litres of blood per minute. This device utilizes an implantable Li-ion battery pack that is recharged through the skin.

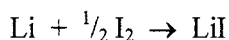
In general, all implantable batteries must have these characteristics [80]:

- Safety (tolerance to electrical and mechanical abuse)
- Predictability of performance (voltage, current, and time relationships)
- Reliability (low variability of performance parameters)
- High energy density (also low battery weight and small battery size)
- Low self-discharge (reduced parasitic reactions)
- End-of-life indication (usually loaded or unloaded voltage based)
- High cycle life and safe charging (for secondaries)

Batteries for the treatment of cardiac diseases include the following: Li/I<sub>2</sub>, Li/Silver Vanadium Oxide, Li/MnO<sub>2</sub>, Li/CF<sub>x</sub> and Li-ion batteries. Li/MnO<sub>2</sub>, Li/CF<sub>x</sub> and Li-ion batteries have been dealt with in Sub-sections 4.7.2, 4.7.3 and Section 5.7, respectively.

### 6.1.1. The Li/I<sub>2</sub> Battery

The basic cell reaction in a lithium/iodine battery is:



The cathode contains a mixture of iodine and poly-2-vinylpyridine (PVP), which when reacted together at high temperature form a conductive, charge transfer complex [80]. In the most commonly used approach to the construction of a Li/I<sub>2</sub> cell, the molten cathode material is poured into the cell and a layer of LiI forms at the anode, producing *in situ* a separator layer. The energy density of the lithium/iodine-PVP system is high, due to the high energy density of I<sub>2</sub> and because separator and electrolyte are not added to the cell. During discharge, the LiI layer grows in thickness, this increasing the cell impedance. Due to the solid electrolyte of the system, Li/I<sub>2</sub> cells typically supply low currents, in the  $\mu\text{A}$  range. This current output has been able to meet the requirements of implantable pacemakers over the last several decades. Additionally, high safety and reliability have made the Li/I<sub>2</sub> cell a good choice as a pacemaker power source. Li/I<sub>2</sub> cells have demonstrated very long life under usage conditions, as illustrated in Figure 6.1 for a pacemaker battery on test for ~10 years. Other larger implantable Li/I<sub>2</sub> battery designs have demonstrated longevity under similar test conditions for over 14 years.

A Li/I<sub>2</sub> battery for implantable pacemakers is shown in Figure 6.2. The smallest battery produced by the pioneer in this field, Wilson Greatbatch



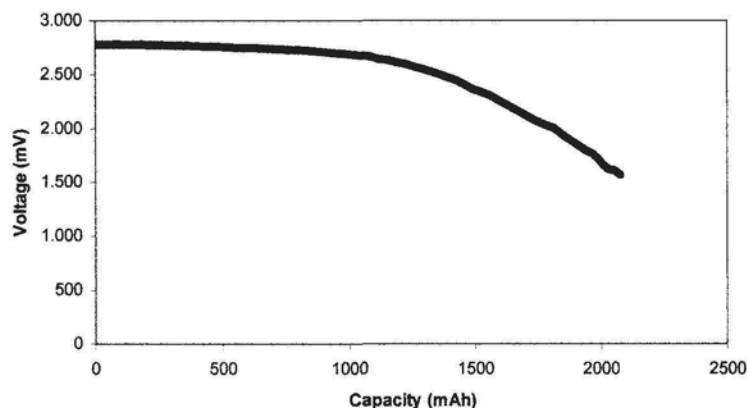


Figure 6.1. Discharge of a lithium/iodine-PVP battery under a 100 kohm load at 37°C. At the beginning of the test, this load corresponds to ~28  $\mu$ A current drain. (From Ref. 80)

Technologies (WGT), has a capacity of ~400 mAh.

### 6.1.2. The Li/Silver Vanadium Oxide (SVO) Battery

The anode of this battery is lithium metal, while the cathode is  $\text{Ag}_2\text{V}_4\text{O}_{11}$

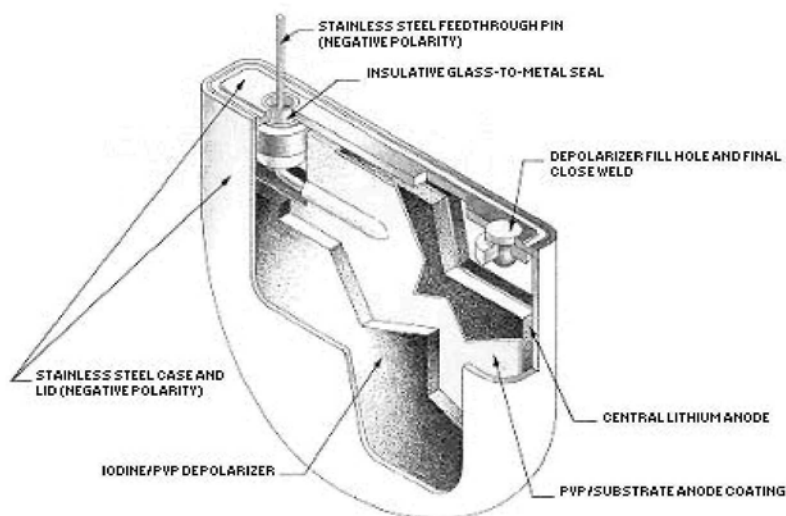
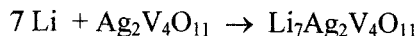


Figure 6.2.  $\text{Li/I}_2$  battery for pacemakers. The case is the positive electrode. (Courtesy WGT)

(SVO). The cell reaction is:



The electrolyte of choice is  $\text{LiAsF}_6$  in PC-DME. Electrolyte additives such as  $\text{CO}_2$  or organic carbonates like dibenzyl carbonate (DBC) have a significant effect on the long term performance of Li/SVO batteries and are believed to reduce internal resistance by modifying the surface layer at the lithium anode.

The addition of 7 equivalents of Li to SVO corresponds to a theoretical specific capacity of 315 mAh/g, this resulting in a specific energy of 270 Wh/kg and an energy density of 780 Wh/L for a practical cell.

The reduction of SVO over the range  $0 < x < 2.4$  for  $\text{Li}_x\text{Ag}_2\text{V}_4\text{O}_{11}$  gives rise to the formation of metallic silver that greatly increases the conductivity of the cathode material, this contributing to the high current capability of the Li/SVO system. At  $x$  values  $> 2.4$  the reduction of  $\text{V}^{5+}$  to  $\text{V}^{4+}$  and  $\text{V}^{3+}$  was identified, and at  $x > 3.8$  mixed-valent materials were found, containing  $\text{V}^{3+}$ ,  $\text{V}^{4+}$ , and  $\text{V}^{5+}$  in the same sample. The presence of several different oxidation states of vanadium, as well as  $\text{Ag}^+$  reduction, results in a stepped discharge curve (Figure 6.3). This step-wise change in voltage provides state-of-charge indication for the implanted battery.

In Figure 6.3, the effect of superimposing current pulses to a background current is shown. The high rate pulses of 2 A were each 10 sec in duration and applied in sets of four, 15 sec apart. As can be seen, a cell submitted to this

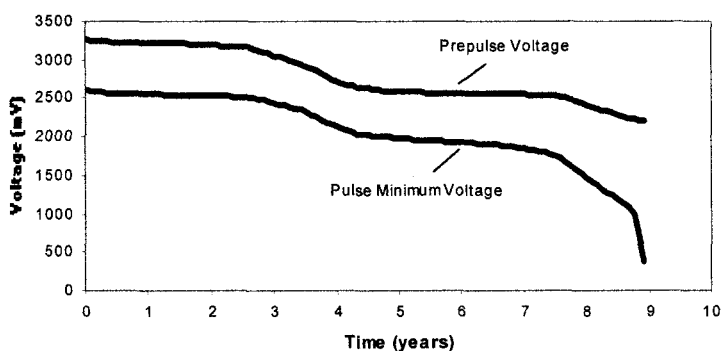


Figure 6.3. Discharge of a lithium/silver vanadium oxide battery under long-life test pulse conditions at  $37^\circ\text{C}$ . Four 10 sec, 2 A pulses are applied every 30 days, with a background load of 100 kohm applied continuously. (From Ref. 80)

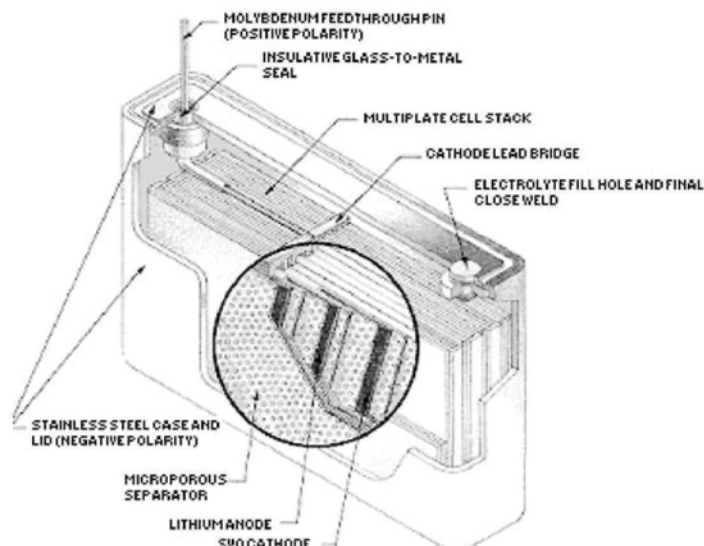


Figure 6.4. High rate Li/SVO battery for ICD applications. The stainless steel case is the negative electrode. (Courtesy WGT)

regime has long life characteristics, with 9 years of real time data collected.

Two types of Li/SVO batteries (by WGT) are available: high rate, capable of Ampere-level current pulses, for cardioverter defibrillators (Figure 6.4), and medium rate, working in the mA range, for atrial defibrillators. As an alternative to the multi-plate design, high rate batteries can be constructed with the spirally wound configuration [81].

Cardioverter defibrillators (see also above) can deliver one or more electric shocks, in 5-10 seconds, to a heart that has started beating too fast. The power of these shocks may be as high as 8 W [81]. The battery is unable to do that but can charge, with currents of 1.5-3 A in 5-10 seconds, the capacitors delivering the shock. Furthermore, the battery must deliver a continuous current in the  $\mu\text{A}$  range and last 5-10 years. The high current charging the capacitor may only be obtained with high-area electrodes. A modern battery for defibrillators has a volume of  $6.6 \text{ cm}^3$  and a weight of 19.3 g. A single cell of 1.35 Ah (spirally wound configuration) can do the job [81].

## 6.2. Other Medical Applications

*Micro-gastrointestinal investigator.* This is a battery-powered diagnostic capsule which, after ingestion, maps the small intestine with a videocamera. The images are transmitted at the rate of two per second to a data recorder, powered by a second battery, carried by the patient [82]. The endoscopy capsule, shown in Figure 6.5, provides photos and streaming videos during its 8-h journey through the digestive system. It basically consists of: light source, camera, processing electronics, data radio transmitter and Zn/Ag<sub>2</sub>O primary batteries. The capsule has the objective of scanning the small intestine which is relatively inaccessible to other non-invasive techniques. The color images so transmitted help identifying such diseases as intestinal obstruction, ulcers, cancer and bleeding. The capsule contains semiconductors of the CMOS type that allow miniaturization and reduce energy consumption.

*Implantable gastric stimulation system.* This pulse generator, implanted under the abdomen's skin, is designed to provide stimulation to the stomach for treatment of obesity (Figure 6.6) [83]. The system also includes an external programmer and a gastric stimulation lead that conducts the pulses to the stomach's smooth muscle. The external programmer communicates with the pulse generator and can modify the electrical parameters. The stimulator has the dimensions of a matchbox (about 5x1.5 cm and 55-60 g) and includes a Li/SOCl<sub>2</sub> primary battery that lasts 2-8 years, as a function of the program applied.

*Self-regulating responsive therapeutic device.* This is a biosensor-drug delivery system which eliminates the need for telemetry and human



Figure 6.5. Left: Capsule components: 1. Optical dome; 2. Lens holder; 3. Lens; 4. Illuminating LEDs; 5. CMOS images; 6. Batteries; 7. ASIC (Application Specific Integrated Circuit); 8. Antenna. Right: Actual size (11x26 mm). (Courtesy of Given Imaging)

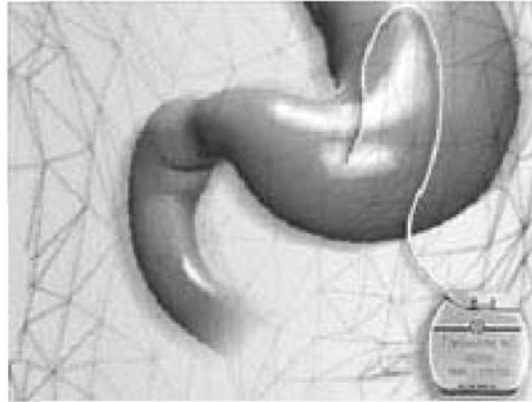


Figure 6.6. Gastric stimulation system. (From Ref. 83)

intervention. Biosensor, electronic feedback and drug releasing mechanism are fully integrated [84]. The heart of the system is a matchstick-sized drug dispensing pill which has rings of hydrogel and polymer. The ring contracts when drug releasing is needed. The batteries powering the system, shown in Figure 6.7, are of the Li-ion type (produced by Quallion LLC, see later) with dimensions of 2.9x13 mm (diameter vs. height). The Li-ion operating voltage, 4.0-2.7 V, is preferable for the operation of the micro-actuators that control the drug release from the reservoir.

*Remote medical diagnosis unit.* This device enables people without medical experience to collect and transmit vital data, *e.g.* blood pressure and heartbeat, to a remote doctor. It can be used on aircrafts, ships or other locations where mains power is not available. A device of this type, Tempus 2000, is

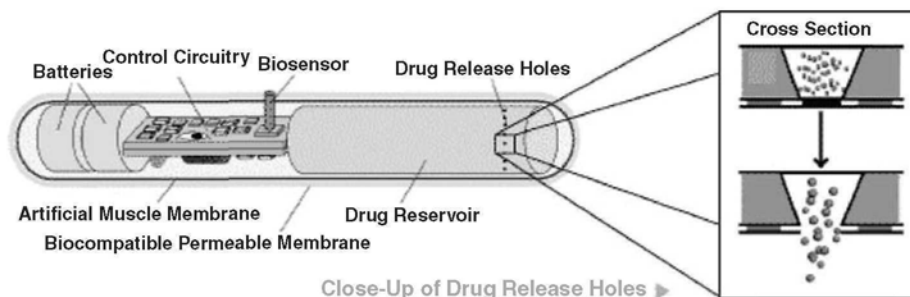


Figure 6.7. Cross-section of a biosensor-drug delivery system. (From Ref. 84)

reported to be powered by a prismatic Li-ion battery (by SAFT) [85]. Such battery has a rated capacity of 24 Ah and a state of charge indicator.

*Implantable microstimulator.* This is a tiny, programmable device which could help victims of stroke, Parkinson's disease, epilepsy, urinary incontinence, *etc.*, by muscle and/or nerve stimulation. The Bion<sup>TM</sup> neurostimulator (shown in Figure 6.8), which can be considered a bionic neuron, has been developed by Advanced Bionics and is powered by a Li-ion battery developed by Quallion LLC in cooperation with Argonne National Laboratories [86]. Due to the very limited dimensions (see figure), the implant requires a minimally invasive operation. The battery has the same size of that used in the self-regulating responsive therapeutic device (see above), so it can be assumed it is the same. The electrolyte is a conducting polymer based on polysiloxane, a Si-containing macromolecule. Polysiloxane is liquid but may be made solid by cross-linking with a second polymer (not disclosed). The thin film so obtained has a similar conductivity, at the body temperature, of the electrolytes used in common Li-ion batteries. The nature of the cathode is not clearly mentioned. In a paper describing a small battery by Quallion for remote sensing applications, the use of  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  is mentioned [87], so it is possible that the same cathode is used in this device. The battery is endowed with a management system (BMS, see also Chapter 7) that control recharging of the battery and remote programming. Recharging is done wirelessly by an external electric field.

The implantable microstimulator is not yet mass-produced. The battery cost is very high for the moment, 400 \$, but would be lowered by mass-production. Other applications of this battery in microelectronics are expected.

*Hearing aids and artificial ears.* In Chapter 4, the Zn/air primary battery was mentioned as the battery of choice for hearing aids. In the last few years, the use of small rechargeable batteries has gained attention, especially in view

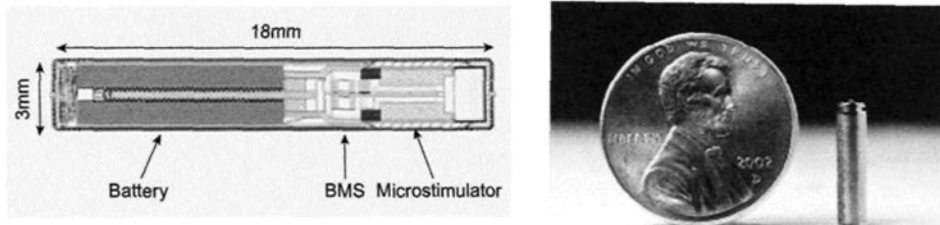


Figure 6.8. Left: Cross-section of an implantable microstimulator. Right: real battery. (From Ref. 86)

Table 6.1. Li batteries and related medical applications.

Battery	Medical Application
Li/I <sub>2</sub>	Pacemaker
Li/SOCl <sub>2</sub>	Drug pump, Microstimulator
Li/CF <sub>x</sub>	Pacemaker, Drug pump, Microstimulator
Li/SVO	ICD, Drug pump, Microstimulator
Li/MnO <sub>2</sub>	ICD
Li-ion (C-LiCoO <sub>2</sub> )	LVAD, TAH, Remote diagnosis, Biosensor- drug delivery, Hearing aid*, Transdermal nerve stimulation*

\* Possible future applications

of the fact that a Zn/air battery needs to be replaced every 5-15 days [88]. A Li-ion battery (C-LiCoO<sub>2</sub>) of the same dimensions of a typical hearing aid Zn/air battery, 312 (see Table 4.6), was tested at the regime of this application. This battery can be cycled more than 2000 times and proves capable of powering a hearing aid for 5 years on a daily use cycle.

A solid state rechargeable Li microbattery has been proposed for the artificial ear, or cochlear, that is an implantable device for profoundly deaf individuals. The battery is: Li/Lipon/LiCoO<sub>2</sub>, where Lipon stands for Lithium Phosphorus Oxynitride, a glassy solid electrolyte. The electrodes-electrolyte assembly can have a thickness of 15 microns and is supported by a metal foil or ceramic or an OEM component [89]. It is claimed to be cyclable for over 60000 cycles and to be usable in a number of microelectronic applications. Radio frequency energy is used to recharge the battery remotely, thus enabling fully implantable product designs. The long cycle life provides permanent power and eliminates the need to replace the battery.

In Table 6.1, Li batteries are listed along with their principal medical applications. A review on the use of Li and Li-ion batteries in present and future medical devices can found in Ref. [80].

## 6.3. Batteries for Special Applications

### 6.3.1. Batteries for Microsensors

The interest in remote microsensors which could operate in an autonomous way, *i.e.* without connection, is steadily growing. Examples include accelerometers, sensors for pressure, temperature, humidity, and

chemical sensors. All these devices can be built on a microscopic scale [90]. An autonomous sensor microsystem has to include the sensor, an (optional) actuator, electronics for data processing and radio-frequency (RF) transmission, and a power source. This has to be not only of microscopic dimensions, but also locally rechargeable. Therefore, a suitable arrangement could be the one shown in Figure 6.9. The batteries can be charged by solar cells, both components having the dimensions of the sensor and associate electronics. Sensors of this type are now frequently referred to as microelectromechanical systems (MEMS), as they integrate silicon-based microelectronics with such mechanical element as sensors and actuators. Microelectronic integrated circuits can be thought of as the "brains" of a system, while sensors are the "eyes" and actuators, if present, are the "arms". Sensors gather information from the environment, the electronics then process the information derived from the

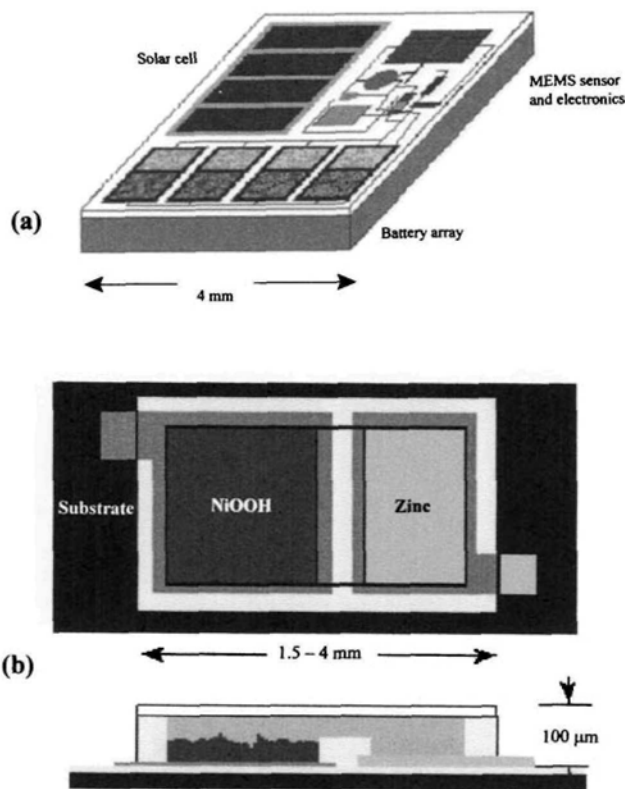


Figure 6.9. Basic drawing of an autonomous microsensor (a); top view and cross-sectional view of cell design (b). (From Ref. 90)



sensors and may direct the actuators to some specific action as moving, regulating, pumping, *etc.* As shown in Figure 6.9, the battery array has a substantially bidimensional shape. To this end, the battery has to be constructed with the same technique used to build MEMS and integrated circuits. Its area should be of a few  $\text{mm}^2$  and the thickness of 0.2-0.3 mm.

During data collection, the battery should deliver powers in the range 0.1-1 mW, and during RF transmission the power should be about 5 mW for a few milliseconds.

Two types of batteries have been so far reported for this application: Zn/NiOOH and solid-electrolyte Li batteries. The former uses an alkaline electrolyte (20% KOH, saturated with ZnO, in  $\text{H}_2\text{O}$ ) and, so, it is very similar to the Cd/NiOOH battery (see Section 5.2). Its most relevant feature is the high power capability allowed by the highly conducting electrolyte. To make this battery integrable in a microdevice, the side-by-side configuration shown in Figure 6.9 was chosen. This design is not ideal from the battery performance point of view, as the electrodes should be stacked one above the other. On the other hand, this design greatly simplifies the fabrication procedure, while the internal resistance is kept reasonably small by the limited dimensions. This battery can be discharged at currents  $>50 \text{ mA/cm}^2$  with a volumetric power density above 3000 W/L. More than 2000 cycles are possible in a typical MEMS regime.

To comply with the requirement of a power of  $\sim 5 \text{ mW}$  during transmission and with the dimensions of the microsensors, the battery should have an area of  $\sim 0.1 \text{ cm}^2$ . This means a specific power of  $\sim 50 \text{ mW/cm}^2$  [91]. The battery described above reaches this goal. Until some time ago, Li-based microbatteries had specific powers well below that value, but the use of more conducting electrolytes and new fabrication techniques have allowed higher powers.

Details on the fabrication of thin-film lithium batteries and their solid electrolytes can be found in Refs. [92,93]. As already mentioned [89], an excellent solid electrolyte for these batteries is lithium phosphorus oxynitride (Lipon). This material is obtained by RF magnetron sputtering of  $\text{Li}_3\text{PO}_4$  in  $\text{N}_2$  with a typical composition of  $\text{Li}_{2.9}\text{PO}_{3.3}\text{N}_{0.46}$ . Its conductivity is  $2 \times 10^{-6} \text{ S/cm}$  at  $25^\circ\text{C}$ , its  $\text{Li}^+$  transference number is 1 (that is, current is only carried by  $\text{Li}^+$ ), and is stable to 5.5 V vs. Li [92].

Based on this electrolyte, several thin-film cells with Li as a negative electrode and different cathodes as positive electrodes have been built and tested. Cathode materials include:  $\text{LiCoO}_2$ , amorphous or crystalline  $\text{LiMn}_2\text{O}_4$ , and amorphous or crystalline  $\text{V}_2\text{O}_5$ . These batteries can be fabricated in various shapes and on different substrates. For instance, they can be added to integrated circuits or to individual circuit components. The fabrication steps include, after

substrate preparation, the deposition of the following films: current collectors (by DC magnetron sputtering), cathode (by RF magnetron sputtering), electrolyte (as above), lithium anode (by thermal evaporation) and parylene/Ti as a protective coating. Figure 6.10a shows a schematic cross-sectional drawing of a thin-film battery. Its total thickness is  $\sim 15\ \mu\text{m}$  [92].

The thin-film battery can be directly assembled on the back of a multichip module of an electronic circuit, as shown in Figure 6.10b. This battery can deliver  $\sim 200\ \mu\text{Ah}$  and 500 cycles at the  $20\text{-}\mu\text{A}$  discharge rate [92].

Apart from microsensors, applications mentioned for batteries of this type are: active EKG (electrocardiogram) electrodes, implantable devices, transdermal drug delivery system, CMOS SRAM and DRAM (static and dynamic random access memory) backup, miniature RF transmitters, smart cards and tags. The last two will be dealt with in the following sub-section.

Lipon is a solid electrolyte belonging to the category of glass electrolytes, the other major category being formed by crystalline ceramic electrolytes [93].

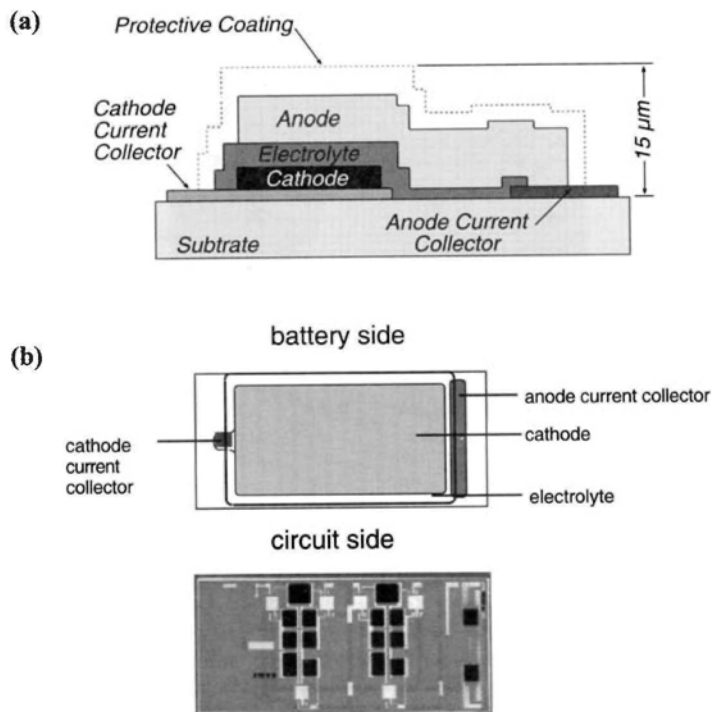


Figure 6.10. Schematic cross section of a thin-film Li battery (a); layout of a Li/LiCoO<sub>2</sub> battery on the backside of a multi-chip module (battery area,  $\sim 3\ \text{cm}^2$ ) (b). (From Ref. 92)

Typical room temperature conductivities of these electrolytes are in the range  $10^{-4}$ - $10^{-8}$  S/cm. However, thin films of 1 mm or less may have sufficiently high conductivities for practical applications. Furthermore, such films may be quite flexible. Apart from an acceptable conductivity, a solid electrolyte has to be chemically and electrochemically stable. This occurs more easily with oxide-based electrolytes than with the sulphur-based ones.

Ceramic and glass electrolytes account for a small percentage of the research work on electrolytes, as attention is clearly focused on the performance of polymeric and liquid electrolytes. For the most part, cells with the organic electrolytes are cheaper and faster to fabricate and have acceptable internal resistance and cycle life due to the advancements in controlling the solid electrolyte layer formed at the electrode-electrolyte interfaces. Although consumer Li-ion batteries will likely continue to use organic electrolytes, other applications may benefit from the introduction of ceramic or glass electrolytes, including applications requiring extreme (high or low) operating temperatures, maximum lifetimes, negligible self-discharge and extremely thin profiles. Of the materials above cited, several stand out as particularly promising, apart from Lipon thin films, *i.e.*  $\text{Li}_2\text{S}\cdot\text{SiS}_2$  glasses stabilized with a small amount of Ta or Sn sulfide, and the partially glassy  $\text{Li}_{1.4}\text{Ge}_{1.6}\text{Al}_{0.4}(\text{PO}_4)_3$  ceramic electrolyte.

Another valuable approach is to create laminated electrolytes using the ceramic or glass electrolytes in conjunction with a liquid or polymer electrolyte. This has been demonstrated using lipon-coated separator membranes, lipon-coated cathode films, and glass-coated metallic lithium anodes. The addition of such a mechanically hard, single-ion electrolyte film to the liquid or polymer electrolyte layer may eliminate the formation of lithium dendrites, inhibit chemical and dissolution reactions of the electrode materials, and reduce the concentration gradients that form due to anion diffusion within organic electrolytes [93].

### 6.3.2. Batteries for Smart Cards and Tags

A smart card is a plastic card containing microprocessor chip(s). It can perform a whole series of functions, such as:

- Biometric identification (face recognition, hand geometry, eye scan, voice recognition, *etc.*)
- Financial data transactions
- Security enhancements: key diversification
- Keypad (also for transportation, parking, mass transit)
- Display

The battery, which has to be thin and flexible, can be embedded in the smart card with a dual function: powering the microprocessor and maintaining the volatile memory. Li batteries based either on solid or polymeric electrolytes are suitable for this purpose, as both can be constructed with thicknesses below 0.3 mm.

Tags can be made active with the use of the same batteries. It is possible now to have RFID (radio-frequency identification) tags in the form of flexible labels or in any other form factors.

### 6.3.3. Examples of Peculiar Battery Uses

Here, a couple of particular applications will be mentioned, as examples of the countless possibilities offered by the new battery technologies.

*Animal cam.* Miniature digital videocameras, powered by thin batteries, can be mounted on wild animals to follow their movements. With this equipment, birds, reptiles and mammals provide images for scientific studies or just documentary programs. The small videocamera shown in Figure 6.11(left) uses a primary Li/MnO<sub>2</sub> thin battery. With a current drain of 130 mA, an operation time of 6-8 hours is granted. The battery is flexible and can be bent to fit the animal, thus resulting quite comfortable to it. The total weight of the system is 50 g. An example of how the equipment is mounted is given in Figure 6.11(right), where a caracal wears a videocamera powered by a 6 V, 1.5 Ah Li/MnO<sub>2</sub> battery [94].

*Central power source for multiple electronic equipment.* There are cases in which several devices are carried out by an individual. An example is offered



Figure 6.11. Left: Miniature videocamera and thin Li/MnO<sub>2</sub> cell. Right: African lynx (caracal) carrying a videocamera in the wild of Namibia. (From Ref. 94)

by a soldier or an explorer in a mission of limited duration. He can bring several devices, *e.g.* transceiver radio, palmtop, infrared equipment for night vision, GPS compass, *etc.* Each component has its own, not interchangeable battery pack, this resulting in a total battery weight higher than necessary. A central power source can substitute for the various batteries. For this purpose, an energy bus can be created, to which all electronic components can be connected and generate the voltage they need through the use of efficient DC/DC converters [95].

For this specific application, Li-ion batteries have been found suitable. Four cells in series have a voltage of 16.8-11.0 V (from full charge to full discharge), and could be coupled with commercially available DC/DC converters having input voltages between 9 and 18 V. The system connects only one battery at a time to the energy bus. When the first battery is flat or fails, the electronics of the system automatically switches to the next battery.

Li-ion batteries have proven superior, in this application, to such primary batteries as alkaline  $\text{Zn/MnO}_2$ ,  $\text{Li/SOCl}_2$  and  $\text{Li/SO}_2$ . Li-ion batteries can provide the required power and energy values at room temperature, but during operations at low temperatures their capacity drops significantly. However, as the energy sources can be kept sufficiently close to the carrier's body, the operating temperatures can be above at least 0-10°C.

## Chapter 7

# BATTERY SAFETY, MANAGEMENT AND CHARGING

### 7.1. Correct Handling

A battery is an energy source and, as such, care has to be used in handling it. The safety level reached by batteries is now very high, thanks to the rules imposed to manufacturers. This is especially true for rechargeable batteries packs, where mechanical and electronic safety devices have been added, as will be later reported in detail. However, risks from improper use may come from any kind of batteries, including the common primary ones. People working in this field use to say that even a beans' can may be dangerous if one heats it in an oven. Similarly, an AA radio battery may cause problems if some simple precautions are not observed. Indeed, the user should be aware that such a cheap battery cannot bear sophisticated safety devices, so that only correct handling may ensure safety. Some warnings are indicated on the label, as mentioned on page 29. Several battery producers publish leaflets and catalogues with detailed handling precautions. Appendix E reports examples of these for different chemistries.

It has been observed that two common misuses include: 1) polarity inversion, and 2) short circuits. The first point is especially common when replacing series- or series/parallel connected batteries in a device [96]. Figure 7.1 provides an example of this misuse. In Figure 7.1a, battery 3 is reversed, so batteries 1-3 are in series and battery 4 is charged. In Figure 7.1b, battery 4 is reversed and closing the circuit will cause its charging. These situations may result, in worst cases, in battery venting, cracking or even exploding.

A polarity inversion may also occur if cells in series have not the same capacity. This may happen when using: cells of the same size but different producers; cells of the same size but different chemistries (*e.g.* Zn-C and alkaline); cells of different sizes; an already partly discharged cell with fully charged cells; a defective cell. In these cases, the cell with the lowest capacity may discharge to 0 volt and eventually be driven into voltage reversal. The heat so generated may cause venting or rupture.

Accidental short circuits may occur if any metallic conductor, such as a key or a piece of aluminium foil or a spiral notebook binder, connects the poles. Once again, while (relatively) expensive cells or packs have internal means to cope with excess current and thermal runaway, cheap batteries are unprotected

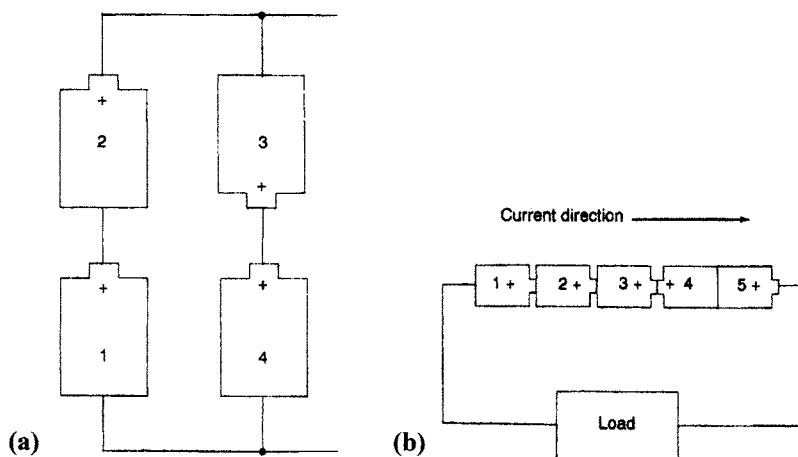


Figure 7.1. Series-parallel circuit: cell 3 is charged (a); series circuit: cell 4 is charged (b). (From Ref. 96)

and damages may result.

## 7.2. Mechanical and Thermal Safety Devices

For the batteries presenting non-negligible levels of safety hazards, safety devices have to be embedded in the cell. Simple mechanical devices and thermally operated mechanisms will be described in this section, while electronic control will be dealt with in the next section.

Basically, mechanical devices are grouped under the definition of safety vent. When an overpressure builds up in a cell, because of either an overcurrent or overheating (the latter may be a consequence of the former), the safety vent helps releasing the pressure. This device may differently be referred to, according to the cell chemistry and shape, as hole, cap, diaphragm or valve. Examples of its location in the cell are given in Figure 1.7. In Figure 7.2, the operation of one of these devices is shown. An overpressure causes the Al lead from the positive electrode to lose contact with the Al disk connected to the external contact. Such a device is used, for instance, in Li-ion batteries.

Examples of thermal devices include the following [97]:

*Negative Temperature Coefficient (NTC) Thermistor*

This device senses the internal battery temperature and provides this information, by means of a calibrated resistance, to an external control circuit.

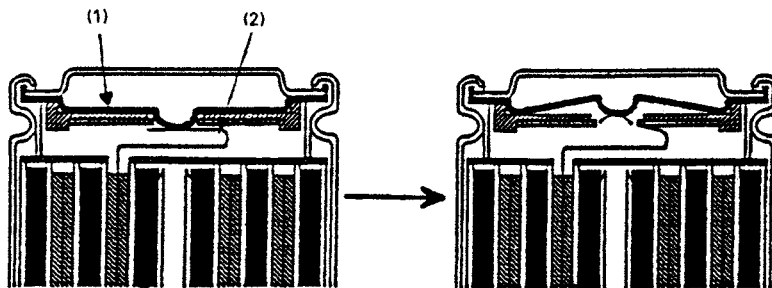


Figure 7.2. Vent mechanism for a Li-ion cell. (1) Aluminum disk, (2) Aluminum lead. An overpressure disconnects disk from lead. (Courtesy of Sanyo)

The resistance varies inversely with temperature. The advantage of this thermistor is that the control can be set outside the battery, so that any temperature variation can be detected and used to control both discharge and charge.

#### *Thermostat*

This bimetal device operates at a fixed temperature and is used to cut off the charge or discharge when a preset internal battery temperature or current is reached. These temperature cut-off (TCO) devices reset automatically after the temperature or current has decreased below a threshold value.

#### *Thermal Fuse*

This device opens the circuit when a set temperature is reached (normally 30-50°C above the maximum battery temperature). It is not resettable.

#### *Positive Temperature Coefficient (PTC) Device*

In this device, the resistance increases with temperature, so that the current flowing through the battery decreases to a safe level. The PTC device responds to high currents (e.g. in short circuits) and acts like a fuse. However, unlike the normal fuse, it resets to its low resistance state when the abnormal current ceases. It also responds to high temperatures around the PTC device, thus acting like a TCO device. Recently, polymeric PTC devices have been introduced (see Section 7.4).

Among the above thermal devices, only the PTC can be enclosed in a single cell. The other ones, and the PTC itself, are used to control a multi-cell battery and, in this respect, their location at critical spots in the battery stack is very important to ensure their correct response. An example of correct positioning of thermal devices is given in Figure 7.3.

Another simple safety device that can be used in battery circuits is the diode. If used in series with a cell or battery, it prevents undue charging, while



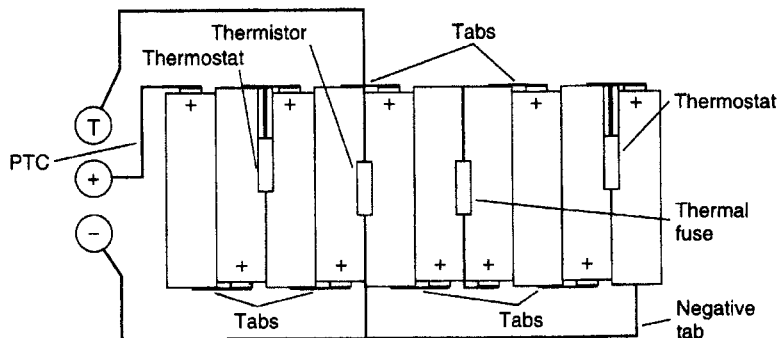


Figure 7.3. Location of safety devices in a cell series. (From Ref. 97)

in series with each cell of a multi-cell battery it prevents voltage reversal.

### 7.3. The Electronic Battery Control

The devices of the previous section help ensuring a safe battery use. However, they are dumb, passive elements giving no contribution to the understanding of the battery state. Furthermore, secondary batteries need some form of management to ensure long cycle life (optimum battery utilization) and user safety. With the introduction of electronic circuits based on adequate microprocessors, battery management has become possible. In particular, charge and discharge are kept under strict control, safety is further improved, and the user can have such information as battery state of health (SOH), battery state of charge (SOC), number of cycles, *etc.* The control electronics may be inside the battery pack (which may be single- or multi-cell) or, alternatively, in the charger or in the device itself.

The protection provided by microprocessor-based circuits is called primary protection, while the passive elements of the previous section provide a secondary protection. However, as will be later reported, in some batteries a primary protection can be ensured by a passive element. This is the case of particular types of Li-ion batteries, where, to reduce cost, the safety circuit has been eliminated and the primary protection relies on PPTC devices [98].

### 7.3.1. Ordinary ('Non-smart') Battery Charge and Management

#### 7.3.1.1. Linear Regulator Chargers (Cradle Chargers)

For some devices, *e.g.* cellular phones, preferred battery charging is done by using a cradle charger in which the device, or just the battery, is placed. The advantage of this method lays in the fact that the heat dissipated by the charger has much less importance with respect to that of a charger integrated in the device. The circuit used in these chargers is a linear-regulator charger, which drops the difference in voltage between the DC power source and the battery across a pass transistor operating in the linear region – hence the name linear regulator [99].

Linear chargers have relatively large dimensions and their efficiency can hardly exceeds 60%. Efficiency is a measure of how much energy the power supply wastes. The heat so generated has to be eliminated with fans or heat sinks. Figure 7.4 shows an example of linear charger. The transistor Q1, external to the integrated circuit (IC), drops the DC voltage to the value requested by the battery and is responsible for most of the power dissipation. Therefore, the IC's temperature remains relatively constant and its internal reference is more stable, this resulting in a more stable battery-voltage limit [99].

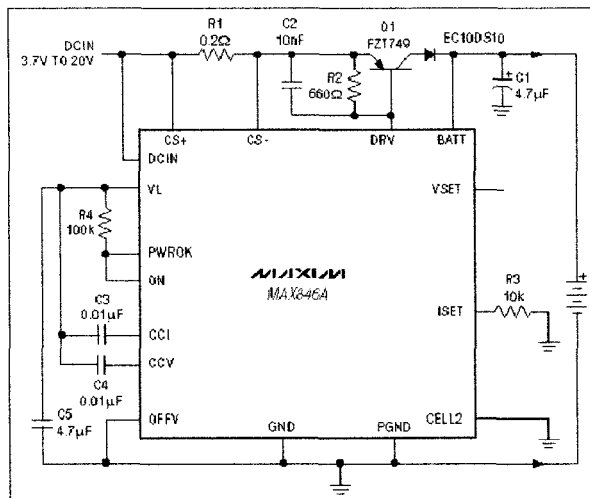


Figure 7.4. Battery charging circuit based on a linear regulator. The transistor Q1 is in the upper-right part of the figure. (From Ref. 99)

### 7.3.1.2. Switching Regulator Chargers (Built-in Chargers)

In some larger devices, *e.g.* notebooks, the battery charger is part of the system and, therefore, heat generation has to be limited. A battery operating at high temperatures is doomed to a short life. A switching charger is remarkably smaller than a linear one and can be embedded in the device. This is so, because it is based on a switch-mode power supply (SMPS) [100]. The SMPS (often called switching regulator) generally consists of a transformer, a pulse width modulator (PWM), a power transistor and feedback circuitry, in addition to switches that are in one of two states, *on* or *off*. Power conversion can be accomplished with minimal power loss, that is the efficiency is high (>80%).

SMPS are 80% smaller and 80% lighter than linear supplies and, while the latter can only step down the input voltage, the former can step down, step up or invert. The main drawback of switching regulators is the noise level generated by their switching action (10000 times more than in linear regulators). However, there are means to cope with this drawback, *e.g.* connecting special capacitors from the AC input terminal to earth. A charger of this type, shown in Figure 7.5, needs a passive inductor/capacitor filter (A) to convert the switched voltage into the voltage requested by the battery [99]. The microcontroller (B), external to the IC, monitors the battery voltage and shuts off the charger when the set

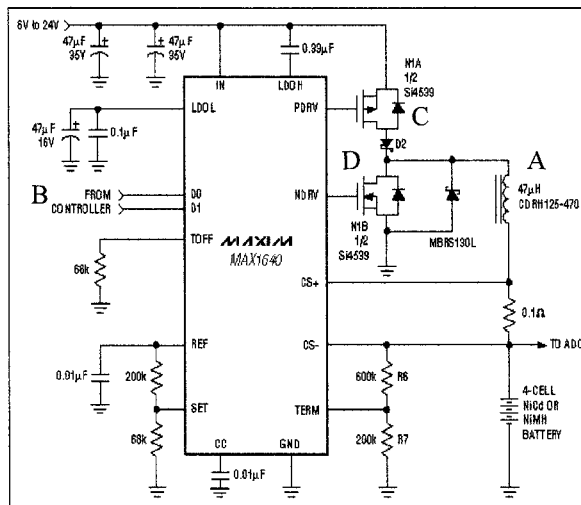


Figure 7.5. Charger for four Ni-Cd or Ni-MH in series, based on a switching regulator. (From Ref. 99)

values are reached. The charger IC chops the input voltage using a switching transistor (C) and a synchronous rectifier (D). This voltage is then sent to the inductor/capacitor (A) and can be used by the battery. The circuit of Figure 7.5 manages 4 Ni-Cd or Ni-MH in series, dividing the charge into three steps: a) constant current fast charge, b) lower constant current top-off charge and c) pulse trickle charge to counterbalance self-discharge.

### 7.3.1.3. The Complete Power Management

Let us consider now the complete circuit including battery, battery charger and portable device. A simplified block diagram is shown in Figure 7.6 [100].

The main functional blocks are: 1) voltage regulation; 2) battery management; 3) load management.

AC/DC converters, DC/DC converters and low dropout (LDO) regulators carry out the function of voltage regulation. AC/DC converters (adapters) may use either linear or switch-mode power supplies. The AC line of 115/220 V is converted, through the AC/DC converter, into a lower voltage power supply and/or charges the battery. The power from the AC/DC converter or the battery feeds SMPS DC/DC converters and/or LDOs, from which regulated voltages can be drawn. To give an example, a Li-ion battery pack with three cells in series can deliver a variable voltage of 12.6-7.5 V. The V regulators can transform it into constant V outputs of, for instance, 5, 3 and 2 V. It is remarkable that in the last few years the output of the DC/DC converters has been steadily declining, thanks to the progress in microprocessor technology. Converters with output of 2 V or even less are becoming more popular than those of 5 V [101]. Intel has recently introduced a Processor-M in the low-voltage and ultra low voltage versions [102]. The former can work at 1.15 or 1.05 V, in maximum performance mode or battery optimized mode, respectively. The latter can work at 1.10 or 0.95 V, in the above modes. These values allow low power consumptions and, at the same time, excellent performance in notebooks [102]. Low-voltage DC/DC converters now feature power efficiencies higher than 94%.

Battery management (the second block) is described throughout this chapter. The main function of the third block, load management, is to shutdown power in parts of the host that are in stand-by in order to reduce energy consumption. Other features, such as overcurrent protection and slew rate control, may be present [100]. The latter refers to the use of an IC to control the rate (several V/ms) with which a transistor's voltage is changed.

Improvement of the microprocessor technology has enabled integration of the three blocks of Figure 7.6, for an efficient power management, into a single

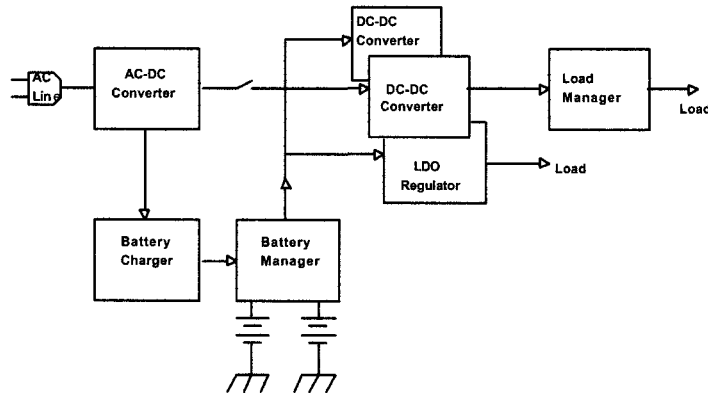


Figure 7.6. Block diagram of a generic power management system. (From Ref. 100)

chip of small dimensions. Philips has recently introduced into the market a power management unit contained in an 8x8x1 mm chip. The chip contains a battery management system, 8 software-programmable power supplies, a battery charger, a 10-bit analog to digital (A/D) converter, up to 3 low-voltage DC/DC converters and 5 LDO voltage regulators with parallel, low current LDOs, and touchscreen interface. This unit, intended for smart phones, PDAs and other handheld devices, can reduce power consumption up to 70%, thus extending battery life. It operates from a pack containing 3 Ni-MH (or Ni-Cd) cells or a single Li-ion cell [103].

### 7.3.2. The Smart Battery System and the System Management Bus

For an intelligent battery management, the battery has to communicate with its host device and with its charger. This can be accomplished with the System Management Bus (SMBus) defined by Intel Corporation in 1995. This system, mainly used in personal computers for low-speed system management communications, is the basis for the Smart Battery System (SBS).

Specifications of the SMBus can be found in the SBS Implementers Forum\* ([sbs-forum.org](http://sbs-forum.org)). Version 1.0 of these specifications was issued on

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\* The Forum is formed by these companies: Duracell, Energizer Power Systems, Fujitsu, Intel, Linear Technology, Maxim Integrated Products, Mitsubishi Electric Semiconductors, PowerSmart, Toshiba Battery, Unitrode, USAR Systems.

February 15, 1995 and version 2.0 (the last, to the best of the author's knowledge) on August 3, 2000.

The term *battery management* basically refers to any battery subsystem using electronics to manage and report the SOC, ensure charge/discharge control and increase the battery safety. The driving force towards the development of smart batteries was the need to provide optimal charge control. An additional factor was the need to control individual cells in multi-cell batteries to keep a proper balance of the cell voltages.

The objective behind the SBS was to transfer the charge control from the charger to the battery. With an efficient SMBus, the latter becomes a master, tells the former, acting as a slave, about its chemistry, voltage and size, and thus dictates the algorithm. The battery controls such parameters as voltage, current, switching point, *etc.* [104].

The term *smart battery* may include rather different degrees of control. Some batteries are claimed to be smart just because they talk with an IC. The IC may only identify the battery chemistry and tell the charger which algorithm to apply. The SBS forum would hardly define these batteries as smart, as they should at least provide SOC indications. Smarter batteries can control overcharge and overdischarge; even smarter batteries provide more controls and information, this obviously adding to the battery cost. There are some smart battery standards, but defining a smart battery has to take into consideration a specific application [104].

In 1990, Benchmarq was the first company to produce an electronic circuit able to detect the battery SOC. Several companies are now producing more or less sophisticated circuits for smart batteries. They range from the single wire system to the two-wire system of the SMBus [32].

The single wire system uses only one wire for data communications, as shown in Figure 7.7a. In addition to the two battery terminals, an additional wire (thermistor) allows for temperature sensing. This system stores the battery code and provides readings of T, V, I, and SOC. It is relatively cheap and finds application in some transceiver radios, camcorders and portable computers. Most single wire systems have different shapes and cannot give standard measurements of SOH (see page 178). Indeed, these measurements are only allowed when the hosting device is coupled to a designated battery pack. The original battery has always to be used, otherwise incorrect readings are obtained. Using the single wire system in a universal charger (*i.e.* a charger for all kinds of batteries) is not recommended.

The two-wire SMBus is the most complete system and represents the largest effort to create a standardized communications protocol and smart battery data set (SBData). In this system, data and clock have separate wires, as

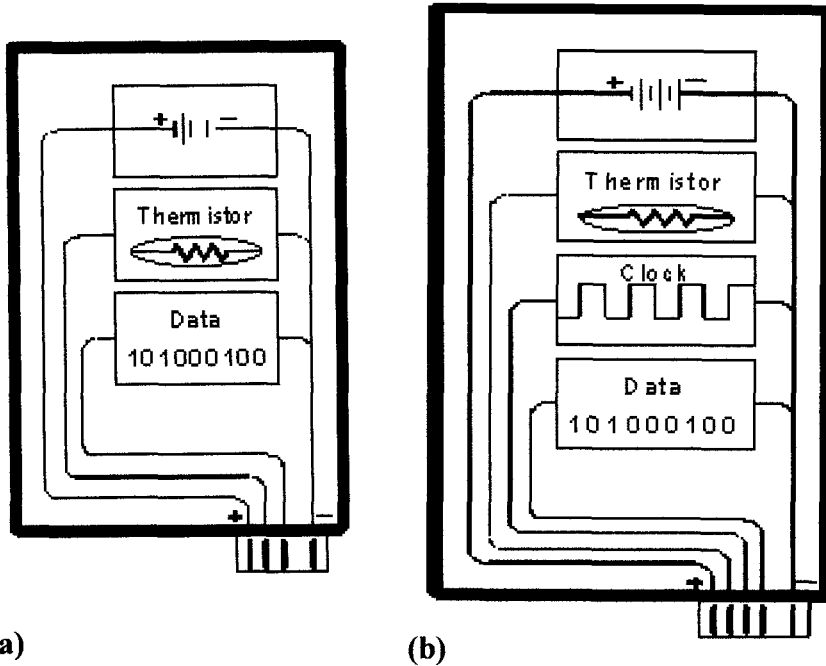


Figure 7.7. Single wire system of a smart battery (a); two-wire SMBus system: clock and data wires are separated (b). (From Ref. 32)

shown in Figure 7.7b. It can be used in universal chargers, as each battery, regardless of its chemistry, would receive the correct amount of charge, as indicated by its specific end of charge characteristics.

An SMBus battery contains permanent and temporary data. The former are encoded by the manufacturer and include battery ID code, serial number and type, manufacturer's name and date of manufacture. Temporary data, *i.e.* cycle number, user pattern and maintenance requirements, is acquired during battery usage.

Full SBdata implementation includes: 1) execution of all data value functions; 2) meeting the accuracy and precision requirements of all data functions; 3) maintaining the proper SMBus timing and data transfer protocols [105]. The data values can be divided into the following categories:

- Historical and identification
- Measurements
- Capacity information
- Time remaining

- Alarms and broadcasts
- Mode, status and errors

Carrying out measurements at a sampling rate allowing a sufficient accuracy is crucial. The rate needs to be higher when a high current is flowing through the battery.

The SMBus is divided into level 1, 2 and 3. The first one is not used anymore, as it did not permit chemistry independent charging. Level 2 SMBus allows battery charging within the host (*e.g.* a laptop computer); the charging circuit may be contained in the battery pack. Level 3 is enclosed in full-featured external chargers. Of course, chargers with level 3 SMBus are sophisticated and expensive. To cut the cost, some chargers with this bus may be not fully SBS compliant. However, in very demanding applications, such as biomedical instruments and precision data collection devices, full compliance is necessary [104].

In Figure 7.8, a smart-battery compliant charger (level 2) is shown. The circuit contains both a switching regulator (with a power efficiency of 90%) and a linear regulator (the latter operating at low currents only). If the input voltage is much greater than the battery voltage, transistor Q1 (A) off-loads the power dissipation. The high switching frequency (250 kHz) of the controller IC (MAX1647 in this case) permits the use of a small inductor (B) [99].

The elements of a complete circuit for battery safety and managements can be better understood with the help of a block diagram (Figure 7.9) [106]. In particular, attention should be given to:

- The IC to protect the battery (a Li-ion in this case) against overvoltage during charge, undervoltage during discharge and excess current
- The thermal fuse (secondary protection): it activates when the cell temperature reaches 90°C
- The discharge and charge FETs (Field Effect Transistors), for charge and discharge cut-off (typically, 4.3 V and 2.5 V):
- The battery resistance sensor
- The fuel gauge (synonymous of indicator of the state of charge) IC, containing, among other elements, the SMBus with separate clock and data lines, temperature sensor, analog-to-digital converter, voltage regulator, microcontroller core and secondary safety for V, I and T.

In Figure 7.10, outlining the safety elements of the circuit, the smart charger and the host are included [106]. One may see that battery, charger and host can talk to one another through the SMBus. The main elements are indicated:

- The T pin is a safety signal preventing charging of batteries that are either unrecognized or do not comply with the parameters enabling a safe charge (*e.g.* a correct voltage value)





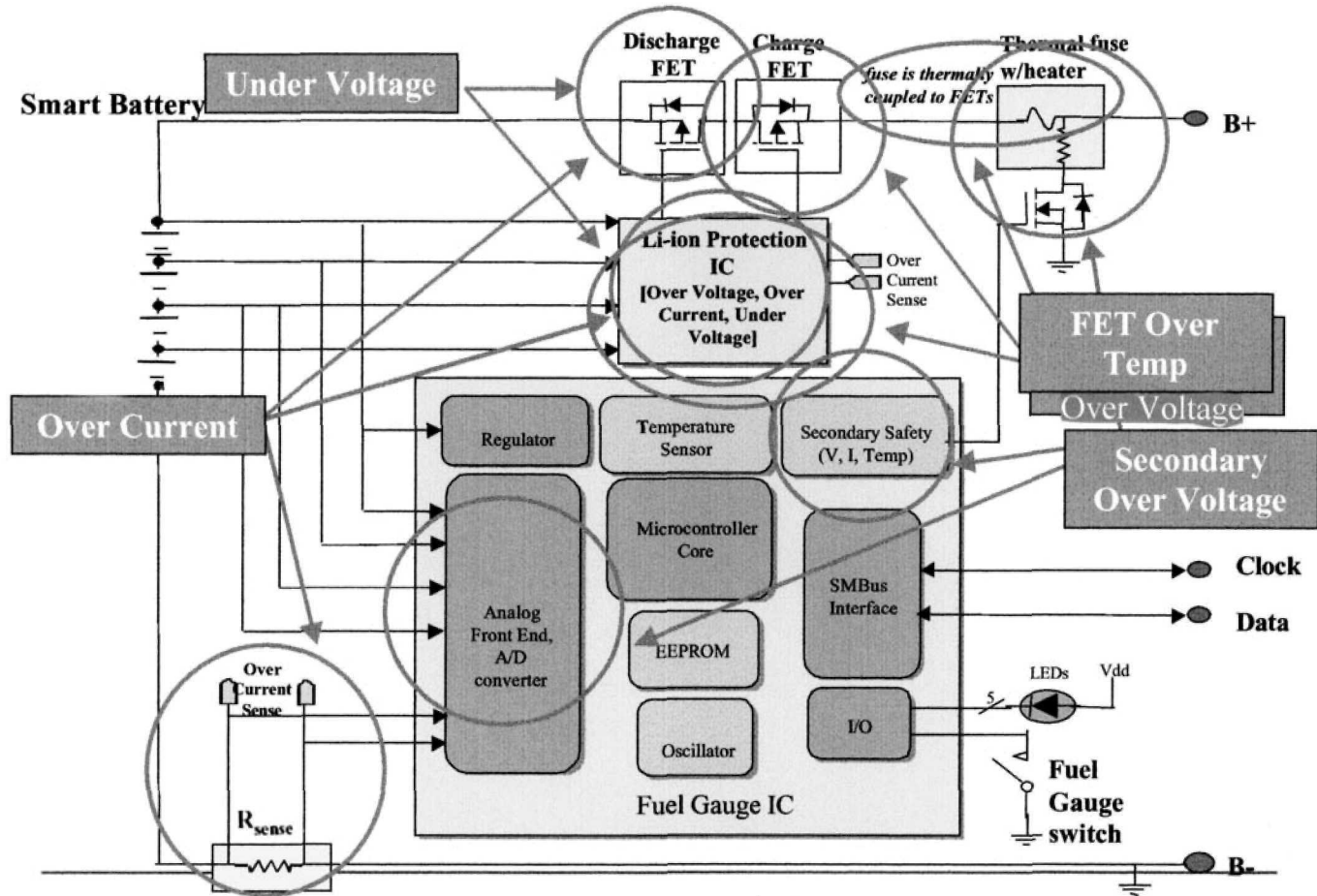


Figure 7.9. Block diagram showing the elements of a smart battery management circuit. (From Ref. 106)

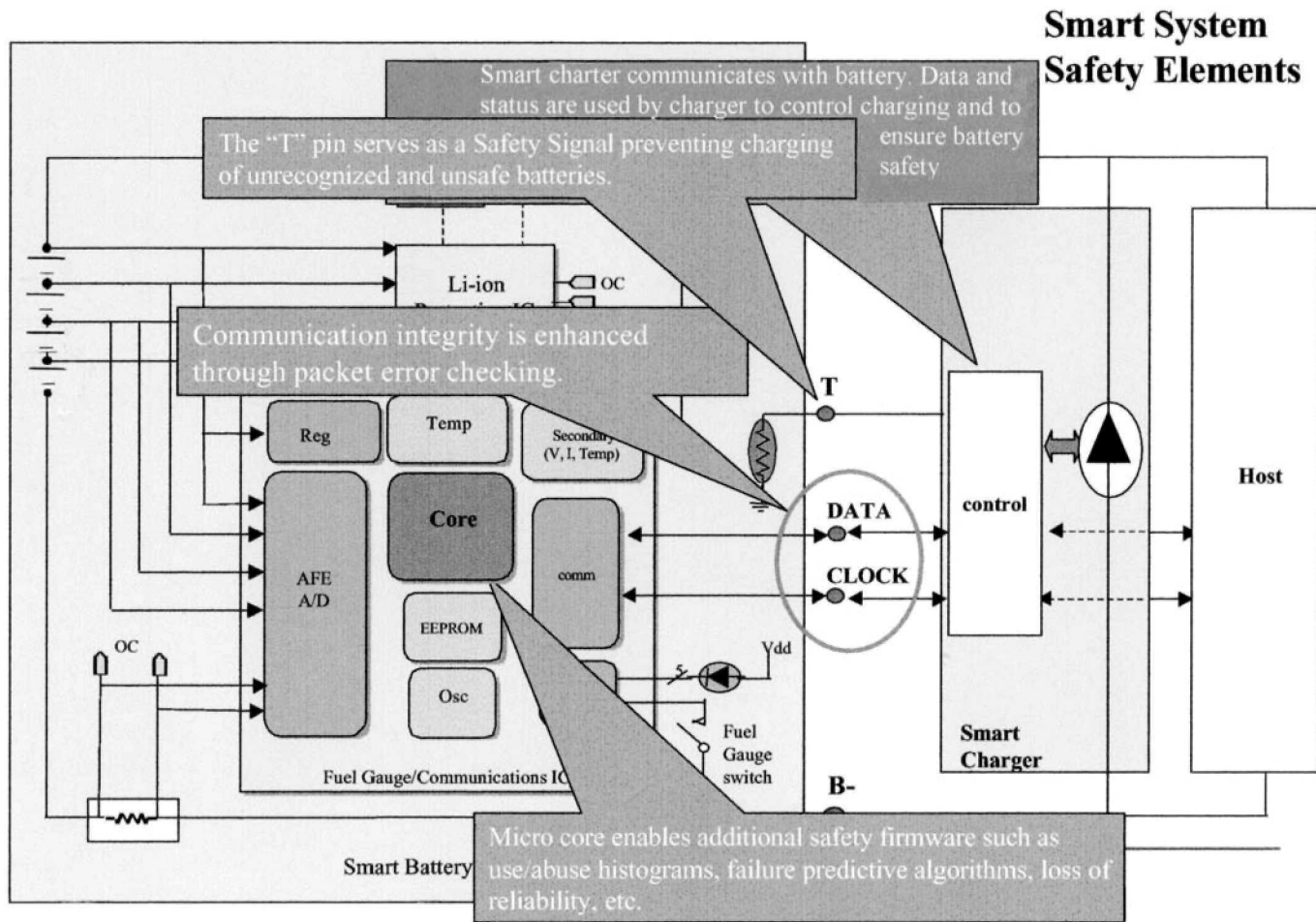


Figure 7.10. Smart system safety elements. The smart charger and the host are also shown. (From Ref. 106)

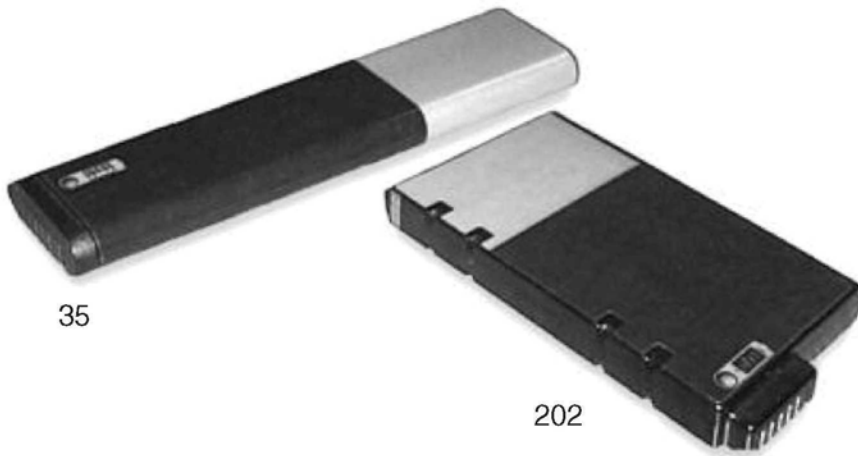


Figure 7.11. Smart batteries with SMBus. (From Ref. 32)

pass through it when the cell is fully charged. This may be accomplished with the use of resistors in parallel with the cell (so-called resistive equalization) [107].

Coming to the practice, two of the most popular batteries relying on the SMBus, are the 35 and 202 series (Figure 7.11) [32]. Manufactured by, e.g., Sony, GP Batteries and Hitachi, these batteries are available in Ni-Cd, Ni-MH and Li-ion chemistries (the latter with full SMBus compliance), and are mainly used for laptop computers, biomedical instruments and high-end survey equipment.

Techniques for measuring the battery capacity are based on measurements of temperature, current and voltage. In any case, a good accuracy is requested to avoid major reading errors. An A/D converter can be used to measure the voltage and to integrate current over time, so determining the amount of coulombs passed. This converter should have at least a 10-bit resolution, that is a sensitivity of 1.6 mV per cell using a 2.5 V reference [108]. Once V and I are measured, the battery characteristics have to be taken into account for an accurate capacity evaluation. In this respect, such parameters as battery chemistry, temperature and discharge/charge rates are especially important.

As shown in Figure 5.37, two Li-ion batteries with the same cathode have different voltage profiles if different C anodes are used. Ignoring this information would give meaningless readings. It is also evident, especially from

the voltage plateau shown by graphite on charge and discharge (Figure 5.37A), that V measurements are not sufficient for obtaining the state of charge and current integration over time is needed.

Another example is provided by Ni-Cd and Ni-MH batteries. Both the rather constant voltage of  $\sim 1.2$  V (Figure 5.14) and the memory effect (depression effect), observed in incompletely discharged batteries, make V readings insufficient for a correct SOC evaluation. In particular, the voltage depression at 1.05 V could stop discharge when only 70% capacity has been delivered. Only a full discharge down to 1.0 V can eliminate this problem and ensure correct capacity readings.

Voltage and capacity values are also a function of the battery discharge (or charge) rate. Therefore, a correct algorithm should consider this factor for each chemistry. Similarly, the temperature affects both the voltage and capacity and has to be measured during operation.

Another effect that should be considered for correct capacity measurements is self-discharge. This is particularly important for Ni-based chemistries and is more significant at high temperatures. The algorithm should calculate the loss of capacity in stand-by conditions, using temperature and time values.

V measurements have to be quite accurate at some charge states. For instance, during the constant voltage charge of Li-ion batteries, a 100-mV change in voltage may result in a 10% higher or lower capacity. If the voltage limit is exceeded, the cycle life can be shortened and if the excess is high, serious safety problems may occur. The overvoltage tolerance is between 25 and 50 mV.

In Section 7.3, the battery state of health (SOH) has been introduced. It could be defined as the fraction of nominal capacity that cannot be recovered as the battery ages. Each battery, either in use or in stand by, ages with a rate depending on the application, the environmental conditions and the way the user treats it. Because of aging, a fully discharged battery cannot be fully recharged. Therefore, the SOC provided by the device is an incorrect value. The correct one may be obtained by subtracting the SOH to the apparent SOC. How can the SOH be measured? In a SMBus battery, the manufacturer set the SOH at the value of 100%. As the battery ages, the capacity delivered is progressively reduced. The battery senses this, so that at any moment of its life the SOH may be indicated (*e.g.* 60% after two years). Based on this, a display can be made indicating the SOC and the SOH, *i.e.* the user is advised not only of the capacity remaining before full discharge is reached, but also of the capacity that is permanently lost. Such a display could be set in an external (level 3) charger [32].

Techniques proposed for measuring the SOC of a battery include voltage recovery [109] and electrochemical impedance spectroscopy [110]. The first technique is based on the  $V/t$  profile on open circuit following the application of a current pulse. The second technique measures the change in cell impedance as a function of SOC.\* The results provided by these techniques are often complex, non-linear and difficult to treat. In these cases, the so-called fuzzy logic methodology may be of great help, as it just helps modelling complex, non-linear systems [104]. The fuzzy logic approach is a generic method applicable to any battery investigation technique. In this approach, the input characteristics of a battery are compared to its output characteristics without taking into account the inherent electrochemical processes. It can be applied to any battery chemistry and may be even used when the available data on the battery are insufficient or intractable with the usual analytical means.

Of course, a treatment of this methodology is out of the scope of this chapter. To give a hint of its background, the following example may be useful. Let us assume that the temperature range 190–200°C is defined as a set of high temperatures. Based on this definition, any value included in this range, *e.g.* 191°C, corresponds to a high temperature, and it has the same ‘membership value’ of another one in the range, *e.g.* 199°C. Using the fuzzy logic, at each temperature a ‘degree of membership’ is assigned, so that, for the above example, 199°C has a higher degree than 191°C. The process of assigning membership values to a set of data is called fuzzification [104].

### 7.3.2.1. Downsides of the Smart Battery

Has the smart battery concept solved all the battery management problems? In fact, there are some drawbacks. The first one is cost: a battery with the SMBus costs about 25% more than its dumb analogue. Furthermore, a smart charger fully complying with the SMBus specifications (level 3) is quite expensive. Therefore, SMBus battery technology is mainly used in higher-level applications.

Another important drawback is the need of periodic calibrations to avoid major errors in the SOC (remaining capacity) measurements. If the fuel gauge could measure the battery capacity at full charge or at full discharge and at constant current, the error would be less than 1% per cycle [32]. As a matter of

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\* The electrochemical impedance of a battery is a complex function of its resistance, capacitance and inductance. It tends to increase during discharge: as the battery approaches full discharge its capability to sustain high current decreases. In other words, its electrochemical processes are slowed down.

fact, a battery may be discharged or charged only partially and a pulse charging technique could be used. Self-discharge upon storage also contributes to an erroneous measurement, as it cannot be accurately compensated by the circuit. To minimize the risk of meaningless readings, a full charge/discharge cycle is needed. A charger enabling full discharge would help in this respect.

What happens if a battery is not calibrated regularly? If the smart charger, as is often the case, is under control of the battery and not of the electronic circuit, the battery will be charged correctly. However, the SOC indication provided by the fuel gauge may not correspond to the real value.

Another problem with the SMBus is that its standardization is not very tight, as some variations in its protocol are allowed. This may cause incompatibility between batteries and chargers, in spite of the fact that the SMBus is just intended to eliminate it.

### **7.3.2.2. Battery Chemistry vs. Management**

The electronic industry now produces a number of ICs for the correct management of batteries according to their chemistry. Original equipment manufacturers make their choice as a function of the performance and price of these ICs. Therefore, they might want just a single chemistry charger (Ni-Cd/Ni-MH or Li-ion or Pb-acid), or a multi-chemistry, smart battery compliant charger/controller.

In Appendix F, commercially available battery chargers, gas gauges, and protection circuits are listed. More details on each of these items can be found on the Internet.

OEMs can take advantage of the performance and price differences among different battery packs, as they can offer multiple choices for the same device. In turn, consumers may select a replacement based on their needs and battery pack cost.

Multi-chemistry charging is now available in several ICs. Two examples of chemistry-independent chargers are: MAX1647 (Figure 7.8) and bq2000 (Figure 7.12). Details on the bq2000 IC are provided here as a way to illustrate how similar ICs work. Bq2000 is a programmable, 8-pin, switchmode IC that can charge Ni-Cd, Ni-MH or Li-ion batteries. The battery chemistry is detected by monitoring the voltage profile in the early charge stages. Afterwards, the fast charge is brought to completion with an appropriate algorithm. The primary charge termination method for Ni-Cd and Ni-MH batteries is based on the peak voltage detection (PVD), while for Li-ion the minimum current charge is sensed (see Section 5.7). A programmable timer is also available to allow a further charge control. Fast charge is not allowed until voltage and battery temperature

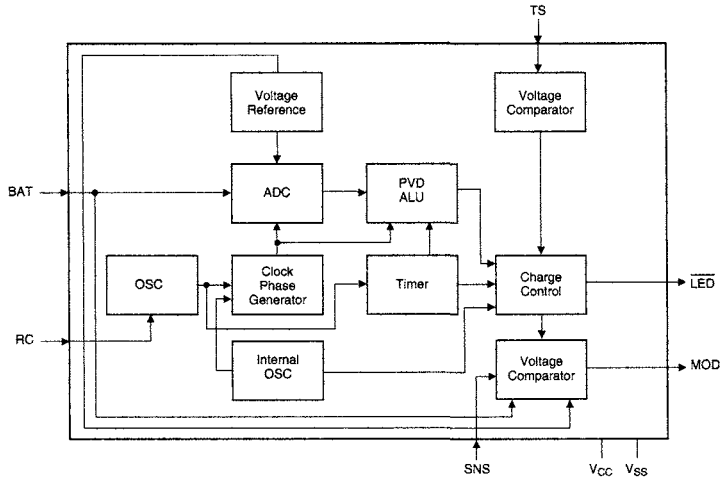


Figure 7.12. Bq 2000 block diagram. (From Ref. 111)

fit in a given range. If  $V$  is low, the IC provides a trickle charge to raise it to an acceptable level. If  $T$  is too high (typically above  $45^{\circ}\text{C}$ ), charge is only started after cooling down; if  $T$  is low (typically below  $10^{\circ}\text{C}$ ), a trickle charge is applied.

The power efficiency is more than 90% and power dissipation is low. Other features of controllers of this type include: sleep mode for low power consumption, battery removal and insertion detection, continuous temperature monitoring and fault detection, user-programmable charge current and voltage [111].

In multi-chemistry chargers, Ni-Cd and Ni-MH batteries are charged at constant current (see Chapter 5) and charge termination is based on voltage, temperature or time values. In the first case, the peak voltage typical of the end of charge is used (Figure 7.13). When the circuit senses a  $V$  variation of a few millivolts with respect to the peak voltage, charge is stopped (see also page 106). The temperature method (Figure 7.14) measures the rate of  $T$  rise ( $\Delta T/\Delta t$ ). If a top-up charge is requested (see page 107), this is made at a lower current and termination is time-dependent. Finally, a trickle charge, usually between  $C/20$  and  $C/100$ , that can compensate for self-discharge, is applied to the battery until it is connected to the management circuit.

For Li-ion batteries, the smart chargers normally apply the constant current (1C), constant voltage (within 1%) method (Figure 5.46). Charge is typically stopped when the current is below  $C/30$  or when the timer tells that time is out. Li-ion batteries have low self-discharge rates, so trickle charge is not



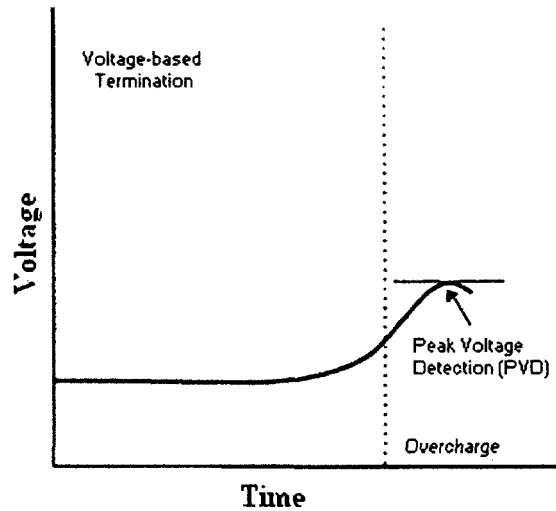


Figure 7.13. Peak voltage detection for charge termination of Ni-Cd and Ni-MH cells. (From Ref. 111)

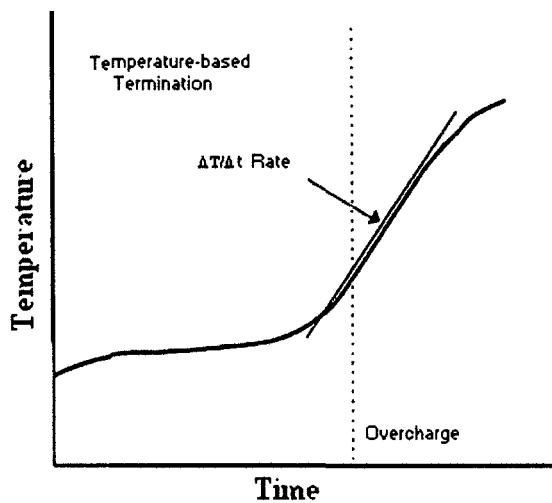


Figure 7.14.  $\Delta T/\Delta t$  detection for charge termination of Ni-Cd and Ni-MH cells. (From Ref. 111)

applied. In any case, this is not recommended as it would overcharge, and possibly damage, the battery. Li-ion packs contain up to four cells: a higher

number would make charging/management too complex. A pulse method has recently been proposed to shorten charge time (see Section 7.5).

#### 7.4. Is Electronic Control Always Necessary?

The cost of batteries with the highest degree of safety/management is 2-3 times higher than that of unprotected batteries. The features of some rechargeable batteries would suggest that, in order to reduce cost, the electronic circuit could be substituted by one of the passive elements of Section 7.2. For instance, this is the case of the recently developed Li-ion batteries based on polymer electrolytes and Mn spinel cathodes. These batteries are intrinsically safer than conventional Li-ion, this prompting some OEMs to rely on polymeric positive temperature coefficient devices (PPTC) for primary pack protection. Low-temperature PPTC devices are considered effective means to protect batteries against external shorts and overcharging [98].

In the PPTCs, a polymer is blended with conductive particles (Figure 7.15). At normal temperature, these particles form low-resistance chains ensuring conductivity. When the temperature exceeds the polymer melting point, that is the device's shut-off temperature, the polymer volume increases and

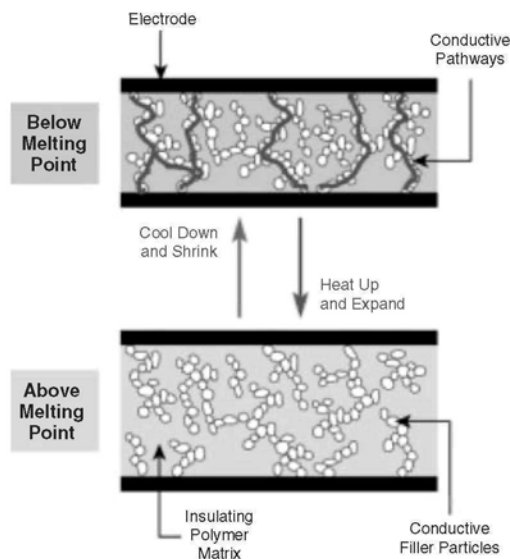


Figure 7.15. Operation of a PPTC device. It passes from a low-resistance state to a high-resistance state in response to over-current or over-temperature conditions. (From Ref. 98)

causes disconnection of the conductive chains. In this way, the device resistance increases by several orders of magnitude. When the cause of overheating is removed, the PPTC returns to its pristine condition, *i.e.* it resets.

Commercial PPTCs can be as thin as 0.5 mm with a typical foot print of 3.3x9 mm, thus being ideal for slim packs. Their initial resistance can be as low as 14 m $\Omega$  and they can sustain a current of 2 A [112].

## 7.5. Examples of Commercial Chargers

In this section, some selected types of chargers will be shown.

Figure 7.16 depicts a charger for Ni-Cd/Ni-MH. It can charge both types (in the AA and AAA sizes) at a time. It uses four techniques for preventing battery overcharge: peak detection, timer, individual cell control, and temperature. This is a classical constant current charger for relatively fast charges (about 2 hours for AA Ni-Cd and about 3 hours for AA Ni-MH).

Recently, chargers based on pulse techniques have also been commercialized. Ni-based batteries receive charge pulses with intermittent discharge pulses to improve charge acceptance. A conditioning button in these chargers allows discharge on demand to get rid of the memory effect: once every month for Ni-Cd and every three months for Ni-MH. A periodic conditioning



Figure 7.16. Ni-Cd/Ni-MH constant current fast charger. (Courtesy of Sanyo)



Figure 7.17. Multichemistry, level 3 charger for SMBus smart batteries. (From Ref. 32)

discharge is also suggested to calibrate SMBus batteries in order to have reliable SOC values.

Smart chargers can also provide an amount of charge selected by the user (e.g. 70 or 80%) to shorten charge time and prolong battery life.

Furthermore, if the battery fails to provide an adequate capacity, the user is advised and battery conditioning starts. If this procedure (basically a full charge following a full discharge) cannot restore the expected capacity, the

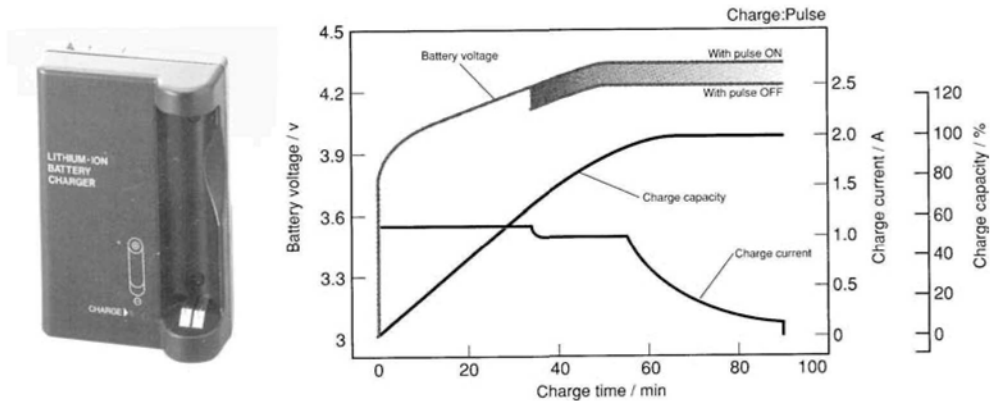


Figure 7.18. Pulse charger (see regime on the right) for a Li-ion pack. (Courtesy of Sanyo)

battery should be replaced. An example of these chargers is shown in Figure 7.17. This multi-chemistry, level 3 SMBus charger can also determine the battery SOH and, so, the correct SOC. Each bay is independent and can charge a Ni-Cd, or Ni-MH or Li-ion battery as it can sense the battery sitting on it and apply the proper algorithm [32].

As already mentioned, Li-ion batteries are normally charged with the constant current, constant voltage technique. At the current rate of 1C, a full charge takes 2-3 hours. To shorten charge time, pulse techniques have been proposed, as in Sanyo's charger of Figure 7.18. According to this manufacturer, 90 minutes are sufficient to reach full charge. Pulse width modulation may also be used: as the battery reaches full charge, the period between pulses increases [113].

The objective of using a pulse current is to increase the rate of electrode reactions. When a sufficiently high charging current flows continuously through a cell, the electrodes become polarized (see Section 1.3). As a consequence, the cell voltage increases and tends prematurely to the upper limit. If the current is stopped for a while, some relaxation may occur, that is the electrodes can have some degree of depolarization and the ionic flux at the electrode/electrolyte interface can be faster.

## **7.6. Safety Tests and Certifications**

The above described safety devices, inside and outside the battery, give the end user an extremely high degree of protection. Nonetheless, few accidents are reported from time to time, especially for Li-ion batteries [114]. In the last few years, the chance of having a happening (such as battery venting) created by a defective Li-ion battery was estimated to one in a million. This incredibly low number still corresponds, with a production of 700-800 million pieces, to 700-800 accidents [115]. During these accidents, a cell might vent (emitting smokes), catch fire or even explode, depending on the underlying problem. Explosion, an extremely rare event, may be complicated by the fact that the iron-based cell housing is being substituted by aluminium housing to reduce thickness and weight [114].

However, not only Li-ion, but also other chemistries have been lately of some concern for users and producers. In 2002, Nikon has recalled digital cameras supplied with alkaline batteries and Siemens has had troubles with aftermarket Ni-based rechargeables, produced by others, for one of their mobile phones.

All batteries and their chargers need to pass safety tests and to receive

certifications before being commercialized. Some international agencies provide the standards for these tests. The major ones are:

- IEC (International Electrochemical Commission)
- UL (Underwriters Laboratories)
- EN (European Norm) of the EU (European Union)
- CSA (Canadian Standards Association)
- TÜV Rheinland/GS

The following tests are normally carried out:

- UL 924 and UL 1989 for VRLA batteries
- UL 1642 for lithium batteries
- UL 2054 for all secondary batteries
- UL 745-3 for portable battery-operated tools
- EN and IEC 60950, UL 1950 for battery chargers

The most general test for secondary batteries is UL 2054. It applies to batteries of capacity below 10 Ahr and to packs constructed with these cells. The tests under this standard are grouped into five main classes: electrical, mechanical, battery enclosure, fire exposure and environmental. In Table 7.1, these tests are detailed for Ni-MH cells and batteries. In the column “Test Results”, experimental evidence by Duracell is reported [47].

The tests for Li-ion batteries (with polymer electrolyte) are reported in Table 7.2 [116].

Altogether, the number and severity of tests ensure a significantly high level of safety to the user. Therefore, the question is: why do accidents occur? First, some batteries have not enough safety devices, as some are erroneously judged redundant. Secondly, some low-cost replacement batteries may have not undergone strict controls.

The Institute of Electrical and Electronics Engineers (IEEE) is creating a “Standard for Rechargeable Batteries for Portable Computers” (IEEE P1625) that will focus on system management and control, battery pack communications, energy density and reliability. In terms of safety of the battery packs, the IEEE P1645 will define even stricter parameters in comparison to those of UL, CSA and TÜV [115].

A specific safety aspect concerns transportation. From this viewpoint, batteries are enclosed in the following categories:

1. *Dry cell batteries: Carbon, Alkaline, Zn/Air, Silver Oxide, Ni-Cd and Ni-MH.*

All these batteries are unregulated for transportation, as promulgated by several organization: US Department of Transportation (DOT), International Civil Aviation Organization (ICAO), International Air Transport Association (IATA) and International Maritime Organization (IMO). In the case of air transport, packaging of these batteries has to ensure prevention of short-circuits.

Table 7.1. Safety tests for Ni-MH cells and batteries. (From Ref. 47)

Test	Test Conditions	Test Results
Flat Plate Crush Test	Cell is crushed between two flat surfaces.	No explosion, sparks, or flames.
Impact Test	A 20 lb. weight is dropped from height of 2 feet on cell.	No explosion, sparks, or flames.
Short Circuit Test*	Sample is shorted until discharged. Test conducted at 20 °C and 60 °C (68 °F and 140 °F).	No evidence of venting, leakage, bulging or other visible changes on individual cells. Maximum case temperature was 129 °C (264 °F). In batteries, safety devices operated, protecting battery from external short. Maximum battery case temperature was within 5 °C (41 °F) of ambient.
Forced-Discharge Test (Voltage Reversal)	The cell, after discharge, is over-discharged for 1.5 times rated capacity.	No venting, leakage, fire or explosion on test conducted at C/3 discharge rate.
Abnormal Charge Test	Cell is charged for 2.5 times rated capacity.	No venting, leakage, fire or explosion on test conducted at C/3 charge rate.
Abusive Overcharge Test*	Sample is charged by power supply up to 200 watts until sample vents or explodes.	Individual cells vented. No explosion or fire. Maximum temperature on cell case was 200 °C (392 °F). In batteries, safety devices caused charging circuit to open periodically, protecting battery as designed. Maximum battery case temperature was within 25 °C (77 °F) of ambient.
Heat Test	The cell is heated in an oven to 150 °C (302 °F).	No damage to cells; no bulging, venting, fire or explosion.
Fire Exposure Test*	Sample is heated by a burner fueled with methane.	Cells and batteries vented without exploding. No significant flaming or spark. No projectiles.
*Note: these tests were conducted on both individual cells and batteries. Tests not marked with an asterisk were conducted on individual cells only, as deemed adequate by UL to demonstrate safety of both cells and batteries.		

## 2. Lead-Acid batteries

These batteries are unregulated for transportation if labelled with the wording "ICAO, IMDG, IATA, and Dot for Air Transport Approved" (IMGD stands for International Maritime Dangerous Goods). The three tests required for the above classification are: a) pressure differential test; b) vibration test; c) A67 Special Provision crack case test per IATA air transportation. The only transportation requirements are the following:

Table 7.2. Safety tests for Li-ion batteries. (From Ref. 116)

**1. Electrical Safety Tests**

Items	Condition	Test Method	Specification	Result
Short Circuit at 25°C	Fully charged	Connecting the positive and negative terminals of the battery with copper wire having a maximum resistance load of 0.1 ohm.	No explosion or no fire; and the temperature of the battery shall not exceed 150°C	Pass
Short Circuit at 60°C	Fully charged	Tests are to be conducted at room temperature and at 60±2°C	No explosion or no fire; and the temperature of the battery shall not exceed 150°C	Pass
Abnormal Charging	Fully discharged	Cell is initially charged at 3C (0.6C) rate by connecting to a 12 V DC-power supply for 48 hours.	No explosion or no fire; and the temperature of the battery shall not exceed 150°C	Pass
Over-charging	Fully discharged	The battery is charged at 1C to 250% of its rated capacity.	No explosion, no fire, no leakage, or no venting	Pass

**2. Mechanical Safety Tests**

Items	Condition	Test Method	Specification	Result
Vibration	Fully charged	Cell is under vibrations of amplitude 0.8 mm, frequency between 10 and 55 Hz, swept at 1Hz/min for 90 min orthogonally in XYZ directions.	No explosion, no fire, no leakage, or no venting	Pass
Shock	Fully charged	Cell is accelerated during the initial 3 msec with the minimum average acceleration of 75 G, and the peak acceleration between 125 G and 175 G, in XYZ directions.	No explosion, no fire, no leakage, or no venting	Pass
Crush test	Fully charged	Cell is placed between two parallel flat steel plates and the electrodes are parallel to the plates, a force of 13 kN is applied	No explosion or no fire	Pass
Impact test	Fully charged	A round rod of 15.8 mm diameter is placed near the center of the cell, parallel to the electrodes and perpendicular to the upper terminal of the cell, and a 9.1 kg weight is dropped from a height of 61 cm to the rod.	No explosion or no fire	Pass
Drop test	Fully charged	Battery is dropped in a free-fall manner for ten times from a height of 1.9 m onto a concrete floor, with arbitrary orientation.	No rupture or ignition	Pass



Table 7.2 (continued)

**3.Environmental Safety Tests**

Items	Condition	Test Method	Specification	Result
Heating Test	Fully charged	The temperature of the oven is to be raised at a rate of $5\pm 2^{\circ}\text{C}/\text{min}$ to a temperature of $150\pm 2^{\circ}\text{C}$ and remain for 10 minutes at this temperature. (1) Raise the temperature from $25$ to $70^{\circ}\text{C}$ within 30 min, and then maintain the temperature for 4 hrs. (2) Reduce the temperature from $70$ to $25^{\circ}\text{C}$ within 30 min, and then maintain the temperature for 2 hrs.	No explosion or no fire.	Pass
Temperature Cycling	Fully charged	(3) Reduce the temperature from $25$ to $-40^{\circ}\text{C}$ within 30 min, and then maintain the temperature for 4 hrs. (4) Raise the temperature from $-40$ to $25^{\circ}\text{C}$ within 30 min, and then maintain the temperature for 2 hrs. (5) Repeat the sequence for further 9 cycles. (6) After 10 cycles, store the cell for 7 days prior to examination.	No explosion, no fire, no leakage, or no venting.	Pass
Altitude Simulation	Fully charged	Cell is left for 6 hours in an environment with an atmospheric pressure of 11.6 kPa.	No explosion, fire, leakage, or venting.	Pass
High Humidity Storage Performance	Fresh cell	After full charge, store at $60^{\circ}\text{C}$ and 90% RH for 30 days.	No gassing and no leakage	Pass
High Temperature Storage Performance	Fresh cell	(1) After full charge, store at $85^{\circ}\text{C}$ for 48 hours. (2) After full charge, store at $90^{\circ}\text{C}$ for 4 hours.	No gassing and no leakage	Swelling less than 2%

- The battery and its external packaging must be labelled “Nonspillable”.
- The battery must be securely packaged in such a way to prevent the possibility of short circuiting

3. *Lithium batteries: primary and rechargeable.*

These batteries are subjected to various transportation regulations that went into effect as of January 2003. Prior to this date, small Li and Li-ion cells and batteries were unregulated. New regulations require testing, as specified by the Amendments to the Third Revised Edition (1999) of the United Nations Recommendations on the Transport of Dangerous Goods. The tests are:

- Altitude simulation
- Thermal cycling
- Vibration
- Shock
- External short circuit
- Impact
- Overcharge
- Forced discharge

It has been stressed that the above tests provide a still uncertain safety, if one fundamental aspect is overlooked, *i.e.* a proper packaging [117]. If at any stage of transportation the batteries become loose, charging, short-circuiting, overdischarges and crushes may occur. It is likely that, in these conditions, the limits observed in normal laboratory tests are exceeded. In 1999, a tremendous fire developed at the Los Angeles airport, when the packaging of lithium batteries was damaged by forklift trucks [117].

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## Chapter 8

# ENERGY SOURCES SUPPORTING, OR SUBSTITUTING, BATTERIES

## A. SMALL FUEL CELLS

### 8.1. Introduction

Portable electronic devices of last generation are based on low-power microprocessors (see also Chapter 7). In principle, this would reduce the energy and power required to the battery. On the other hand, there is an increasing demand of functionality in these devices, so the number of components they contain and the associate power consumption are also increasing. Laptop computers able to provide wireless high-speed communications can be taken as an example. In spite of the progress made by batteries in this field, they are the limiting factor in the runtime of these portable devices. It has been calculated that the highest energy density deliverable by the most energetic battery, Li-ion, is 550 Wh/L. This is very near to the actual limit (see Section 5.7), so, unless an entirely new system emerges, batteries will not keep pace with the progress of electronics.

This consideration has spurred research on fuel cells, a different class of power sources with theoretical energy values well above those of batteries. The basic difference between a battery and a fuel cell is that in the former the energy sources (active materials) and the energy converters (supporting electrodes) are enclosed in the same container, while in the latter the energy sources are continuously supplied to the energy converters. An exception to this definition is the metal/air battery where a reactant is outside the battery case.

One of the reactants of a fuel cell has the characteristics of a fuel, *i.e.* it can give a combustion process with oxygen. In this type of cell, such reaction occurs through reduction and oxidation processes at special electrodes with catalytic properties.

Typical fuels are hydrogen and methanol, which can directly react with oxygen, and natural gas or other fossil fuels, which need to be converted into hydrogen-rich streams before being fed into the cell.

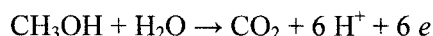
There are several types of fuel cells, but only one has prospects as a power source for portable devices, the proton exchange membrane (PEM) fuel cell that can work at relatively low temperatures, lends itself to miniaturization,

and produces more power than any other fuel cell. Its electrolyte is a polymeric membrane allowing fast transport of  $H^+$  from anode to cathode. If the fuel is methanol, the acronym DMFC (direct methanol fuel cell) is used. At present, only  $H_2$  and  $CH_3OH$  are considered as fuels for PEM fuel cells.

## 8.2. Basics of PEM Fuel Cells

The theoretical specific energy and the energy density of fuel cells using  $H_2$  or  $CH_3OH$  are summarized in Table 8.1. It can be seen that these values far exceed those of the batteries dealt with so far. In particular, for Li-ion batteries, the theoretical values are  $\sim 400$  Wh/kg and  $\sim 1300$  Wh/L.

These exceptionally high energies are remarkably reduced in practical fuel cells, as their complexity is greater than that of batteries. A schematic representation of a PEMFC, in this case with  $CH_3OH$  as a fuel (DMFC), and its basic reactions is shown in Figure 8.1. The fuel contained in a reservoir enters the anode where it is oxidized according to the reaction:



The protons travel through the proton exchange membrane and reach the cathode, where  $O_2$  (from air) gives rise to the reaction:

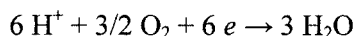


Table 8.1. Theoretical energies of PEM fuel cells.

Fuel	Specific Energy (Wh/kg)	Energy Density (Wh/L)
<b>Pressurized <math>H_2</math></b>	1000	3000
<b>Metal Hydride</b>		
(2% $H_2$ )	650	970
(7% $H_2$ )	2300	3400
<b>Chemical Hydride</b>		
( $NaBH_4$ , 30% solution)	2100	2200
<b><math>CH_3OH</math></b>		
(100%)	6100	4800
( $CH_3OH:H_2O$ 1:1 [M])	4000	3400

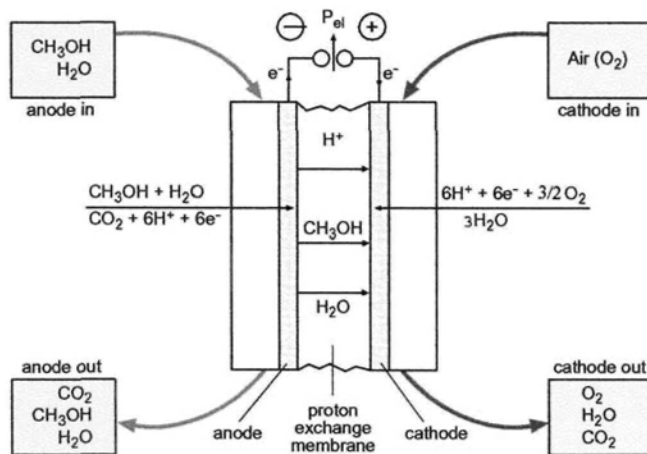
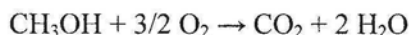


Figure 8.1. Scheme of a PEM fuel cell with  $\text{CH}_3\text{OH}$  as a fuel. (From Ref. 118)

The overall reaction is just combustion of  $\text{CH}_3\text{OH}$ :



Of course, if  $\text{H}_2$  were used as a fuel, the reaction would produce  $\text{H}_2\text{O}$  only.

The basic components of the PEM fuel cell are:

- *The anode.* It has to: provide a common interface for the fuel and the electrolyte membrane, act as a catalyst for fuel oxidation, conduct the electrons to the external circuit or, in case of stacked cells, to a current collector.
- *The cathode.* It has to: provide a common interface for  $\text{O}_2$  and the membrane, act as a catalyst for  $\text{O}_2$  reduction, conduct electrons from the external circuit to the  $\text{O}_2$  reduction sites.
- *The membrane.* It has to: conduct  $\text{H}^+$  from anode to cathode at a good rate (its conductivity has to be high), act as an electronic insulator, keep the reactants separated.

Let us see in more detail the structure and nature of the above components.

The electrodes can be schematically represented as in Figure 8.2. Three layers can be identified: 1) a substrate typically formed by teflonized carbon cloth; 2) a gas diffusion layer, generally formed by carbon particles (size,  $\sim 0.1 \mu\text{m}$ ) and Teflon; 3) an active layer, where the catalyst grains (size,  $20\text{--}40 \text{ \AA}$ ) are supported on carbon (load,  $0.4 \text{ mg/cm}^2$  or less), and the membrane fills the

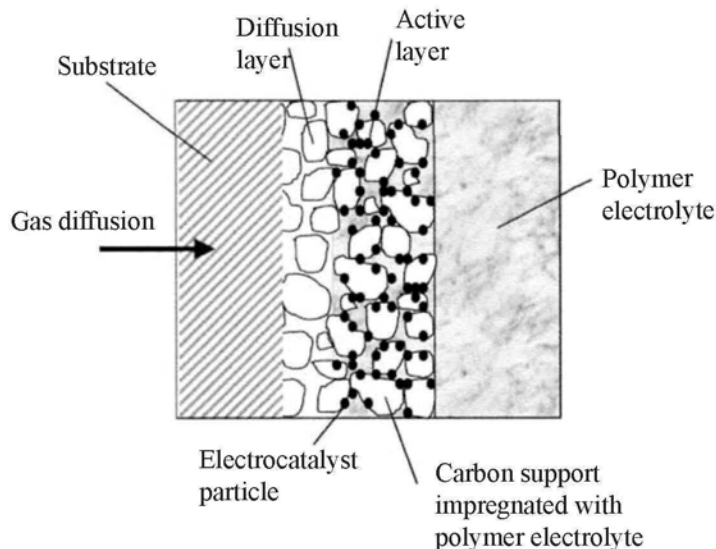


Figure 8.2. Schematic of PEMFC electrodes. (From Ref. 119)

pores [119].

All layers are characterized by a high porosity. Substrate and diffusion layer are electronic conductors, while the active layer is an electronic conductor in the network formed by C and catalyst, and an ionic conductor in the membrane-filled pores. The thickness of the active layer tends to approach 10  $\mu\text{m}$ , and the total electrode thickness is 300–400  $\mu\text{m}$ . The membrane-electrode assembly is called MEA.

The catalyst is Pt when  $\text{H}_2$  is the fuel, while for  $\text{CH}_3\text{OH}$  a Pt-Ru alloy (50%–50%) is preferred at the anode, as it prevents electrode poisoning by CO formed as a by-product during  $\text{CH}_3\text{OH}$  oxidation. The membrane in contact with the catalyst layer is a 10–25  $\mu\text{m}$  thick layer of perfluorocarbon sulfonic acid ionomer. Nafion produced by DuPont is one membrane of this type. Proton conduction in the membrane is due to  $\text{H}^+$  hopping from one sulfonic group ( $-\text{SO}_3\text{H}$ ) to the next one. In the presence of  $\text{H}_2\text{O}$ , sulfonic groups and  $\text{H}^+$  are solvated and this enhances the hopping rate and the conductivity. The specific conductivity of a well hydrated Nafion membrane is 0.1 S/cm at 80°C, *i.e.* about one order of magnitude larger than that of the organic solutions used in Li or Li-ion batteries. The need of having a wet membrane for a good conductivity calls for a proper water management, which can essentially be accomplished in two ways: 1) recirculation of  $\text{H}_2\text{O}$  formed at the cathode; 2) use of humidified

reactants. Water management is also important for the electrodes, where excess water may cause flooding and occlusion of the gas channels.

In the cathode, atmospheric air can be made available through a simple “air breathing” mechanism, *i.e.* diffusion under a concentration gradient, or by forced ventilation, *i.e.* by using a fan. The latter is recommended if a high power output is sought. The use of pressurized air or  $O_2$  is customary in larger cells, but obviously not recommendable in the small ones for portable applications. The combined effect of air pressure and humidity content on the performance of a fuel cell is shown in Figure 8.3. A cell utilizing ambient air and working at 50-60°C, *i.e.* in the conditions encountered by a portable small cell, has a limited rate capability. The conditions applied to the two upper curves refer to relatively large cells (10-100 KW) for transportation. The evidence of Figure 8.3 suggests that an “air breathing” fuel cell has to expose its cathode area to air as much as possible. It will be shown in the following how this can be accomplished.

The trends of the curves in Figure 8.3 indicate the air electrode as the main responsible for the voltage drop under load (polarization). It is interesting to compare the cathode polarization to the contributions of the other cell components. This is done in Figure 8.4 for a  $H_2$ /air fuel cell. The first region, at low current densities, has an exponential behavior and is related to the cathode activation polarization; the second region is almost linear and is connected to

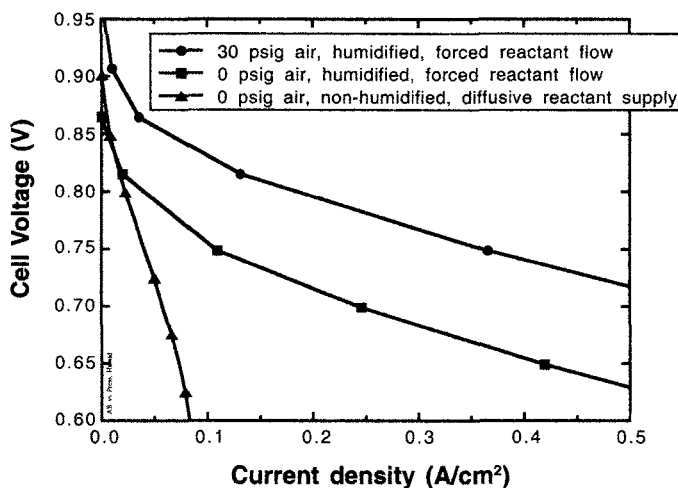


Figure 8.3. Effect of air pressure and its humidification on the polarization of  $H_2$ /air fuel cells. Zero psig = atmospheric pressure. (From Ref. 120)



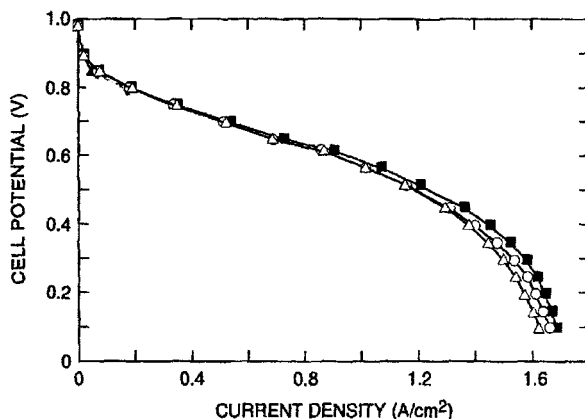


Figure 8.4. Typical V/I curves of a  $\text{H}_2$ /air fuel cell showing three regions of polarization. (From Ref. 121)

ohmic losses in the MEA; the third region is characterized by a steep voltage drop and is connected to concentration polarizations:  $\text{H}_2\text{O}$  transport in the membrane and air transport in the cathode may become too slow to sustain the required current densities.

### 8.3. Single Cell and Cell Stack

The open circuit voltage of a  $\text{H}_2$ /air cell is 1.23 V and that of a  $\text{CH}_3\text{OH}$ /air cell is 1.21 V, but the operating voltages are lower because of polarization phenomena. The operating conditions, *i.e.* temperature, amount of catalyst, humidity, gas flow rate and pressure, also determine the voltage under load. When  $\text{H}_2$  is used as a fuel, the voltage for a given load is slightly higher than that of  $\text{CH}_3\text{OH}$  because of the higher intrinsic activity of the direct hydrogen anode process. Anyway, operating voltages are in the range 0.5–0.8 V, well below those of batteries. To reach the necessary voltage and power outputs, practical fuel cells are made of stacks of single cells, as schematically shown in Figure 8.5.

A fundamental element of the stack is the bipolar plate. It has multiple functions: electronic conduction, delivering of the fuel and air through flow channels on opposite membrane surfaces, prevention of mixing of the reactants, and dispersion of the heat generated during cell operation. Stacked cells and the interleaved bipolar plates are shown in Figure 8.6a. The different paths for fuel

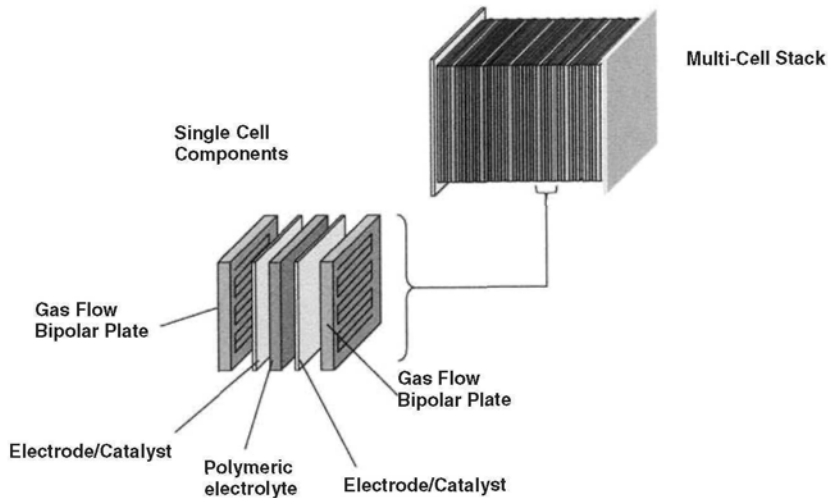


Figure 8.5. Schematic of a single fuel cell and multi-cell stack. (From Ref. 121)

( $H_2$  in this case) and  $O_2$  are evidenced. The electrons generated at the anode are conveyed to the cathode through the plate, while  $H_2O$  generated at the cathode can exit through the plate channels [123].

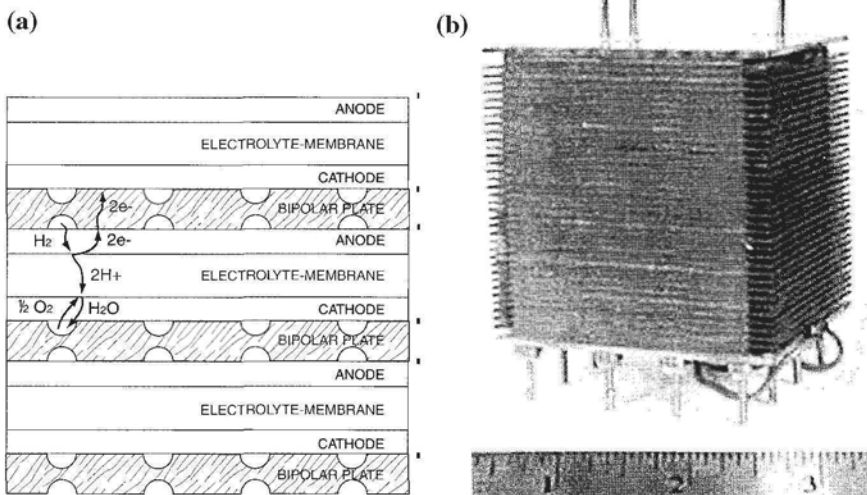


Figure 8.6. Schematic representation of the elements of a fuel cell stack (a), and real cell (b). (From Ref. 122)

A real fuel cell stack is shown in Figure 8.6b. It can be noted that the bipolar plates have finned extensions to better dissipate heat. The use of a small fan powered by the stack itself helps in this respect. Graphite-based plates are preferred in small fuel cells as they are electrochemically stable and have a high thermal conductivity. A polymeric resin is enclosed (less than 20%) to ensure impermeability and improve mechanical properties. In small cells, the thickness of the plate can be as low as 1 mm.

PEM fuel cells work at temperatures from ambient to about 80°C. Too high temperatures cause membrane dehydration and insufficient H<sub>2</sub>O at the anode for the oxidation reaction, while sub-ambient temperatures may cause electrode flooding and, below 0°C, water freezing in the membrane.

The number of single cells to be stacked depends on the power characteristics. A H<sub>2</sub>/air fuel cell recently proposed for powering a portable computer is based on four single cells only. The voltage and power trends of this cell vs. current are presented in Figure 8.7. The cell voltage, after the initial fast decay, remains linear up to 20 mA and affords a power output of 45 W at this current. With the use of a 90%-efficient DC-DC converter, a power output of more than 40 W at 12 V is possible [123]. However, the accessories of the cell, *i.e.* pumps and control electronics, draw part of this power. In the present example, these parts consume about 10% of the power.

The fuel cell complexity can be reduced to some extent, this resulting in performance losses. For instance, the fan can be eliminated, but then the cell has

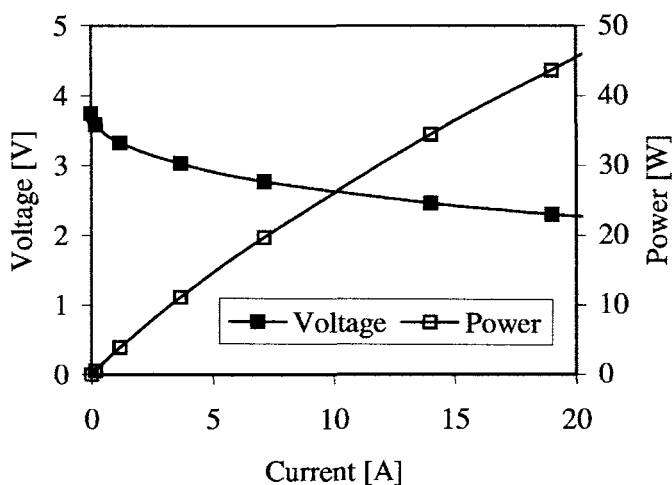


Figure 8.7. Polarization characteristics of a H<sub>2</sub>/air fuel cell. Hydrogen stored as metal hydride. (From Ref. 123)

to work at low power to limit heat production. Similarly, the water re-circulation pump, which brings  $\text{H}_2\text{O}$  from cathode to anode, can be eliminated if one uses a DMFC with hydrated  $\text{CH}_3\text{OH}$  (Figure 8.8). Of course, this results in a penalty as less fuel is available in a given container volume. In the last few

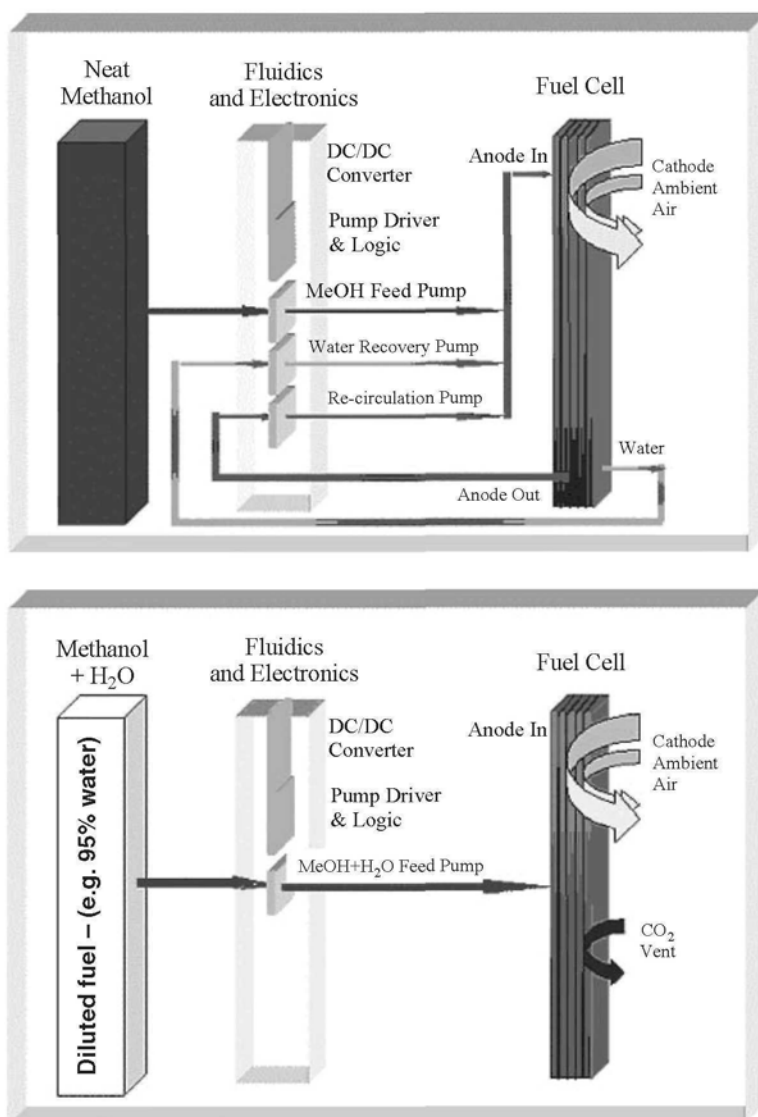


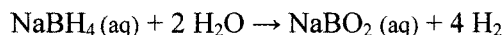
Figure 8.8. DMFC with pure  $\text{CH}_3\text{OH}$  as a fuel and elaborate flow control subsystem (up) and with hydrated  $\text{CH}_3\text{OH}$  and simplified control (down). (From Ref. 124)

years, the technological advances have been remarkable and the issue of reducing the impact of the accessory parts (fluidics and electronics) has been particularly addressed. A leader company in this field claims utilization of a simplified control while using pure methanol, as  $\text{H}_2\text{O}$  would be transferred from cathode to anode within the fuel cell [124].

The methanol container of Figure 8.8 is just a replaceable cartridge whose volume is a function of the runtime requested to the fuel cell. For instance, a 125-ml cartridge is reported to give up to 7 hours of runtime to a 25-W cell.

When hydrogen is used as a fuel in small cells (below 100 W), a convenient way to store it is as a hydride. Metal hydrides are compact and easy to operate. A typical metal hydride uses an  $\text{AB}_2$ -type alloy, where A is, for example, Zr or Zr-Ti, and B is a mixture of transition metals (see also Ni-MH batteries in Chapter 5). These alloys have useful hydrogen pressures at room temperature and 500 Wh/L have been demonstrated in prototypes, while the specific energies are in the range of 200-300 Wh/kg. The containment for the alloy (canister) and other accessory parts decrease the energy obtainable. Once the hydride has fully released its hydrogen content, the canister can be substituted by a charged one (as for the methanol cartridge) and the depleted canister can be recharged [125].

Instead of metal hydrides, chemical hydrides can be used. These have higher specific energies as the amount of hydrogen that can be released is higher. A convenient chemical hydride is  $\text{NaBH}_4$ . Its reaction with  $\text{H}_2\text{O}$  is:



A solution containing 30%  $\text{NaBH}_4$ , 3%  $\text{NaOH}$  and 67%  $\text{H}_2\text{O}$  has 6.6%  $\text{H}_2$  by weight [126]. The reaction needs a catalyst and produces humidified  $\text{H}_2$  ready for the fuel cell. As the reaction is exothermic, no heat input is necessary. This kind of fuel is also called ‘hydrogen on demand’, as  $\text{H}_2$  is generated only upon application demand. The energy densities (Wh/L) are lower than those of metal hydrides because of the lower densities of the reactants.

It has been calculated that 0.45  $\text{cm}^3$  of a 30%  $\text{NaBH}_4$  solution are necessary to produce 1 Wh. At the cost of 28 \$/kg of  $\text{NaBH}_4$ , 1 Wh can be obtained with 0.004 \$ [126]. However, as later pointed out, other items make the overall cost much higher.

Recently, the possibility of storing  $\text{H}_2$  in carbon nanotubes is receiving much attention and some studies report high levels of stored  $\text{H}_2$ .

## 8.4. Technical Challenges in Fuel Cells for Portable Electronics

A power system based on a fuel cell that is designed for a portable device should fit entirely in this device. That is to say that not only the cell stack, but also the accessories have to be accommodated in the limited space presently filled by a battery. The full system must provide the reactants to the electrodes, do water and thermal management, handle the load and regulate the voltage. As is obvious, these prerequisites pose tremendous technical challenges, which will be briefly discussed here.

In Section 8.2, the issue of air transport to the cathode has been introduced. A portable device, *e.g.* a cellular phone or a portable computer, would like to rely on passive air breathing, *e.g.* without any fan or compressor. In this case, all the cathode area has to be exposed to the air, or the oxygen diffusion from the exterior to the reaction sites will be insufficient at high rates and/or long operation times. The situation is worsened in a DMFC working at relatively low temperatures. Indeed, in this case, the presence of liquid  $\text{H}_2\text{O}$  at the anode may increase its content in the membrane and cathode, this hindering  $\text{O}_2$  transport.

If all the cathode area has to be exposed to the environment, a calculation can be made of its value for a fuel cell designed to power a 20-W laptop computer [127]. In case of  $\text{H}_2$  as a fuel, an area of  $31 \text{ cm}^2$  is needed to ensure that the cell can deliver the requested peak power. If  $\text{CH}_3\text{OH}$  is used, at  $70^\circ\text{C}$  and without any forced ventilation, the area becomes  $400 \text{ cm}^2$ . Allocating a fuel cell with this area inside a computer is really problematic: a position external to the computer is more realistic. This has indeed been done in prototypes fuel cells (see pages 207-8).

Let us consider now the problem of the fuel choice and its delivery to the cell stack. The huge theoretical specific energy of  $\text{H}_2$ ,  $32700 \text{ Wh/kg}$ , cannot be approached in real life, as hydrogen has to be stored as metal or chemical hydride. In this way, most of its energy is lost and, in the practice, the energy of methanol is superior. However, as already mentioned, this fuel has oxidation kinetics slower than that of  $\text{H}_2$  and this entails an increase of the cell size and a larger heat production. Furthermore, if a high  $\text{CH}_3\text{OH}$  concentration is used to enhance the cell energy, its oxidation is incomplete (formaldehyde can be formed) and excess  $\text{CH}_3\text{OH}$  can give rise to the crossover phenomenon, *i.e.* it diffuses from anode to cathode through the membrane.

Methanol crossover can be tackled by regulating its concentration at the anode. As is obvious, this is quite easy if the cell provides a constant power output, but any increase in power demand, that would require a corresponding

increase of the rate of  $\text{CH}_3\text{OH}$  feeding at the anode, would make this troublesome. Alternatively, a barrier layer could be inserted in the cell, but this would increase the resistance and lower the power.

Water balance is another matter of concern. The PEM requires  $\text{H}_2\text{O}$  to have a good conductivity: a dry membrane manifests a significant ohmic drop.  $\text{H}_2\text{O}$  is also necessary at the anode for the oxidation reaction of  $\text{CH}_3\text{OH}$ . However, as already noted, if excess  $\text{H}_2\text{O}$  is delivered to the anode, this can raise the  $\text{H}_2\text{O}$  concentration in the membrane and the anode may be flooded.  $\text{H}_2\text{O}$  is also necessary in  $\text{H}_2$ /air fuel cells, although not necessary for the electrochemical reactions, to keep the membrane wet. Basically, water management is the same with both fuels: excess  $\text{H}_2\text{O}$  has to be removed from the cathode and part of it has to be fed to the anode, while dissipating most of it to the outside. All this has to be accomplished within the constraints of a portable device.

Thermal management, already mentioned as regards the water content in the cell, is of the outmost importance also in terms of dissipation of the heat produced. The efficiency of a fuel cell is not very high, mainly because of the poor kinetics of the cathode ( $\text{O}_2$  reduction). The maximum efficiency can be set at  $\sim 50\%$  (but it is much lower for DMFC). This means that a fuel cell delivering 1 W of power to a device will also release at least 1 W of heat to the environment [127]. This is more than that of a battery, whose power efficiency is above 80%. Therefore, one has to provide additional means of heat dissipation in a device or, alternatively, operate at lower fuel cell powers.

A battery responds immediately to a power request. In particular, there is no appreciable delay in the start-up of a device. A fuel cell can manifest problems in this respect. For instance, a completely dry system will require some seconds to produce  $\text{H}_2\text{O}$  at the cathode and to make it available for the anode and membrane. A delay would also be observed at low ambient temperature. This could be tackled, for instance, with a small auxiliary battery able to deliver the requested power until the fuel cell gets ready for takeover. A situation of insufficient response of the fuel cell also occurs in case of sudden load variations. As seen above, this would require a faster fuel feed at the anode, and some time has to elapse. Once again, it seems that an auxiliary battery could better manage the power transients.

Overall, the complexity of the fuel cell system seems to be a serious hurdle to its implementation. At the current development stage, the better way to exploit its potentialities is in connection with a battery. The latter can tackle the power peaks, while the former may recharge the battery and handle ordinary (limited) loads.

## 8.5. Fuel Cells Miniaturization

The present status of technology makes rather improbable constructing miniature fuel cells for portable devices by just scaling down larger cell designs. A new approach is necessary, based on a new technology allowing size reduction of the cell stack and its accessory parts. Ceramic technology seems to suit this purpose with particular reference to the low-temperature cofired ceramic (LTCC) technology disclosed by Motorola [128]. With it, micro-fuel cells of 0.1-1 W have been built, which can be used for PDAs or cellular phones. The fuel cell could power these devices in a steady-state mode, *e.g.* under conditions of low power consumption, in association with a battery that could handle the power peaks. Alternatively, the micro-fuel cell could only be used to recharge the battery.

Starting from a ceramic single cell with an active area of  $4 \text{ cm}^2$ , a 4-cell stack can be constructed. It is able to provide a power output of 100 mW operating with passive air breathing, *i.e.* without forced ventilation. A schematic of the direct methanol micro-fuel cell and its accessories is shown in Figure 8.9. Pure  $\text{CH}_3\text{OH}$  is diluted to 1 M (5%) with water, as this is the concentration allowing the maximum efficiency for the oxidation reaction, and then pumped through the micro-channels with piezoelectric micro-pumps. These are based on the micro-electromechanical system (MEMS) technology mentioned in Chapter 6. As in larger fuel cells, a fluidics and an electronics section are present, but at

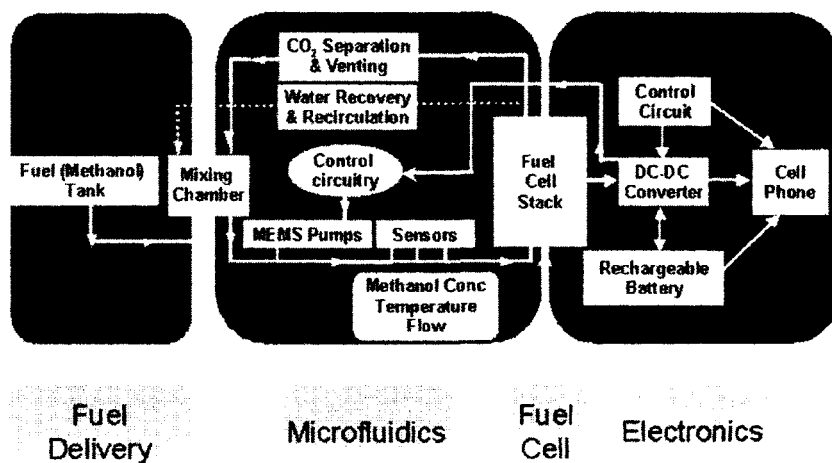


Figure 8.9. Schematic of a micro-DMFC. (From Ref. 128)



the micro-scale level. The electronics includes the battery that forms part of the hybrid system. The 100-mW fuel cell together with its accessories has a volume of 166 cm<sup>3</sup> including fuel. It is able to deliver a constant power of 100 mW for six days without refuelling. Even after miniaturization, the fuel cell is too bulky to fit a space inside a PDA or a cell phone. At present, such a cell seems best suited as an external charger, for instance a holster charger, for batteries.

It has been calculated that even with the smallest available accessories half of the power produced is consumed by the so-called balance-of-plant. The power budget for a 100-mW fuel cell is shown in Figure 8.10. Fortunately, many of the same accessories can be used in a 1-W cell, so minimizing their impact on the power output.

## 8.6. Fuel Cells Prototypes

Several companies have announced the development of prototypes that could be commercialized. Toshiba, Casio, NEC, Smart Fuel Cell (SFC), Jet Propulsion Laboratories (JPL), Motorola, MTI Micro-fuel Cells, Millennium Cell (MCEL) have described different prototypes and technologies.

Toshiba announced in October 2003 a fuel cell to be soon commercialized, but later the launch was postponed to 2005. It is a DMFC for powering portable computers with an average power of 12 W and a maximum of 20 W. The prototype, shown in Figure 8.11, has the following basic

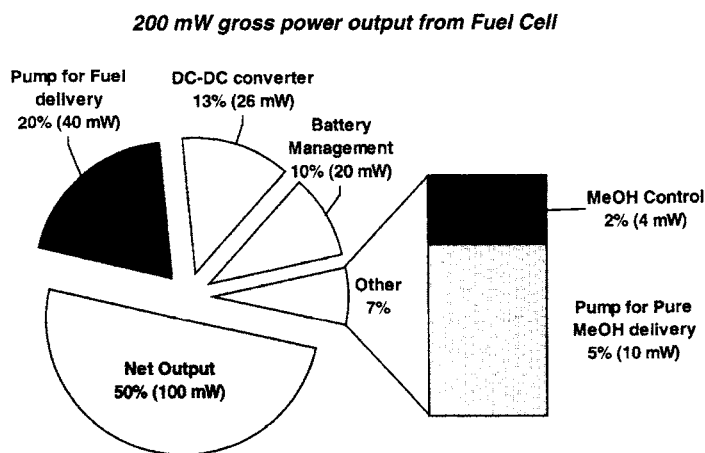


Figure 8.10. Power consumption of micro-fluidics and micro-electronics sections in a 100-mW micro-fuel cell. (From Ref. 128)



Figure 8.11. Toshiba's prototype of a DMFC (left) and its application in a portable computer. (right) (From Ref. 129)

characteristics. Voltage: 11 V, weight: 900 g, volume: 825 cm<sup>3</sup>, cartridge weight (50 cm<sup>3</sup>): 72 g, 5 hours of operating time with a 50-cm<sup>3</sup> CH<sub>3</sub>OH cartridge [129]. Based on these data, a specific energy of 62 Wh/kg and an energy density of 68 Wh/L may be calculated. These values do not compare well with those of Li-ion batteries (see Section 5.7).

Concentrated methanol is used in Toshiba's DMFC and the dilution is made by recirculation of water produced by the cell. A control circuit enables dialog between the cell and the computer, so that power demand and supply are balanced.

The latest announcement by Toshiba is for a 1-W fuel cell with a runtime of 20 hours on a 25-cm<sup>3</sup> CH<sub>3</sub>OH cartridge.

On August 2003, NEC has presented a prototype notebook powered by a DMFC (Figure 8.12, left) [130]. The NEC's fuel cell is said to have an output density of 40 mW/cm<sup>2</sup> and an average output of 14 W (with a maximum of 24 W). Its weight is 900 g and can operate the computer for 5 hours with a 300-cm<sup>3</sup> CH<sub>3</sub>OH cartridge (at 10% concentration). This fuel cell has electrodes made of carbon nanohorns, a variety of carbon nanotubes, with numerous needle-like extrusions having diameters of 2-3 nm. Attaching Pt catalyst to these extrusions, NEC has expanded the surface area of the electrodes, this resulting in higher power generation efficiency.

Fujitsu has presented in January 2004 its fuel cell prototype for a portable computer (Figure 8.12, right). It has a power of 15 W and a run time of 8-10 hours with a CH<sub>3</sub>OH cartridge (30% concentration, 300 g).

It has to be stressed that the price of these prototypes is around 300 \$. On the other hand, a battery pack providing a run time of 7.5 hours for a similar computer costs 45 \$. This clearly excludes, for the time being, a real competition between batteries and fuel cells.

The only European company claiming commercial production of low-

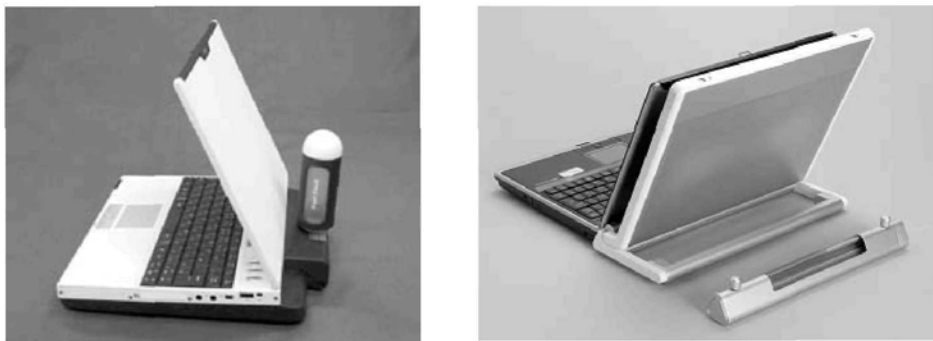


Figure 8.12. Left: portable computer powered by a NEC fuel cell. Right: portable computer with a Fujitsu's fuel cell. (Courtesy of NEC and Fujitsu)

watt fuel cells is SFT (Germany). Their fuel cells are meant for recharging batteries powering portable computers, camcorders, digital cameras and measuring instruments. Their main product, commercialized since September 2003, is a DMFC weighing 9.7 kg, with a power of 25 W at 12 V. Running on a 2500-cm<sup>3</sup> CH<sub>3</sub>OH cartridge (2.2 kg), it delivers its power for 100 hours and is able to provide power peaks up to 80 W [131]. A smaller fuel cell (1.1 Kg, 20 W, 125-cm<sup>3</sup> CH<sub>3</sub>OH cartridge, about 7 hours of runtime) will probably be commercialized by the end of 2004. Apart from the use of 100% CH<sub>3</sub>OH, no other details on the construction of these fuels cells are disclosed.

A list of fuel cell producers/developers is reported in Appendix G.

At the Fuel Cell Seminar held in Miami Beach in November 2003, the DMFC was judged as the most credited candidate for replacing batteries in portable electronics. Methanol is available and cheap, while economic production of hydrogen is not behind the corner. However, the DMFC, according to several experts, maintains its status of 'not yet ready for prime time'. The main issue hindering large commercialization is performance durability. Such factors as methanol crossover, surface oxidation of the catalyst, changes in the water absorption properties of the cathode, and ruthenium crossover may shorten the fuel cell life [132].

Safety issues stemming from the fuel may be added. It is not pleasant going around with relatively large cartridges of CH<sub>3</sub>OH, which is volatile, flammable and toxic. The containment of H<sub>2</sub> is also a matter of concern. It may be foreseen that air transportation of fuel cells and cartridges will be highly restricted.

## 8.7. Comparison of Batteries and PEM Fuel cells

Because of the developmental stage of small fuel cells, a comparison with batteries has some areas of uncertainty. However, in many instances the profiles of the two power sources are clear enough and allow at least a qualitative comparison (Table 8.2).

As already pointed out, the difficulty of fuel cells in managing high loads suggests the utilization of hybrid systems, where the potential high energies of fuel cells could be exploited. However, most of the theoretical energies are lost because of the low efficiency of the systems. A DMFC using pure methanol has a theoretical energy density of 4800 Wh/L, but with a 20% efficiency this value drops below 1000 Wh/L. Recently, an optimized cell design is claimed to bring CH<sub>3</sub>OH utilization to 86% and efficiency to 27% [134]. It will be difficult to attain in practice more than 800 Wh/L for DMFC, a value not largely superior to the limit anticipated for Li-ion batteries (550 Wh/L). For fuel cells using metal hydrides, only 450-500 Wh/L are expected [15,133], in spite of the higher

Table 8.2. Qualitative comparison of batteries and PEM fuel cells. (From Ref. 133)

Attribute	Batteries	Fuel cells
Configuration	Monopolar	Bipolar
Power Density	Very large dynamic range	Limited dynamic range
Specific Energy and Energy Density	Depends on system; maximum for Li-ion	At present lower; room for improvement
Cost	Relatively low	Relatively high
Recharge Time	Minutes to hours	Seconds to minutes
Start-up Time	Micro- to milli-seconds	Seconds to several minutes
Efficiency	Above 80%	Below 50%
Design	Relatively simple	Complex
Environmental Impact	Toxic and flammable components often present	Relatively benign

efficiency for  $H_2$  oxidation (about 50%). If the present energy densities values of fuel cells and batteries are compared, the situation appears particularly favorable to the latter. As already mentioned, a prototype near to commercialization has 68 Wh/L [129].

The most difficult comparison between the two types of power sources is about cost. Even for advanced fuel cells prototypes, this attribute is not clearly mentioned. The use of air at the cathode and of cheap materials like methanol or  $NaBH_4$  at the anode would suggest affordable costs at least for these fuel cells. However, the prices of two basic components of the MEA (membrane-electrode assembly) are quite high: the Pt catalyst is priced at 16 \$/g and the membrane at 800-1100 \$/m<sup>2</sup>. With these values, catalyst-membrane cost for a PDA or a cell phone is expected to be 8.8 \$, and that for a laptop computer 175 \$ [135]. Projections of costs as low as 800 \$/kW appear too optimistic, especially in view of the fact that present costs can reach 20000 \$/kW [15]. Indeed, for a 1-kW cell based on  $H_2$ , a cost of 5000 \$/kW has been calculated [133], but scaling down to cells providing the power for portable electronic (from less than 1W to about 50 W) entails a cost increase. There is no comparison at the moment even with the most expensive battery, the Li-ion one, whose price is decreasing (see Table 5.1 and Chapter 10).

As reported above, the response time of fuel cells may be not adequate for some applications, especially if DMFC with pure methanol is used. This again suggests the convenience of hybrid systems [133,136].

Fuel cells have certainly a point as far as recharge times are concerned, as the mechanical substitution of the fuel container may take few seconds vs. several minutes or hours for recharging batteries. Another point in favour of fuel cells is their impact on the environment. Only  $H_2O$  and  $CO_2$  (the latter for DMFC) are released. However, release of hot water vapor near the user may certainly be unpleasant.

## **B. SMALL SUPERCAPACITORS**

### **8.8. Introduction**

In some applications, relatively low and constant currents are demanded to the battery. In these cases, the most significant battery parameter is its stored energy (Wh). In some other applications, peak powers are requested to accomplish some functions, *e.g.* in a cellular phone during transmission. In these cases, the power (W) characteristics become very important.

Quite often, either the battery is unable to sustain certain peak levels or it can do that at the expenses of its runtime: repeated high-current pulses shorten the battery life. As the power demand of modern portable electronics become more pressing, the need of separating the energy source from the power source has been considered. A capacitor may complement the battery taking care of the current pulses, while the battery can handle ordinary current levels and recharge the discharged capacitor.

Traditional capacitors have long been used in electronic circuits, but they have a serious drawback, *i.e.* the energy contained in their power pulses is too low for many applications. In other words, they can deliver high power in a very short time, in the order of milliseconds, while sometimes several seconds may be requested (see, *e.g.*, cardioverter defibrillators on page 152). For these applications, capacitors with higher energy, also called electrochemical capacitors (EC) or supercapacitors, have been developed. Supercapacitors bridge the energy gap between batteries and conventional capacitors, as illustrated in Figure 8.13 [137]. The energies of electrolytic capacitors is normally well below 0.1 Wh/kg, while commercial supercapacitors can reach 5 Wh/kg and higher energies are provided by particular types (see later). On the other hand, ECs can deliver powers in excess of 1000 W/kg, thus satisfying

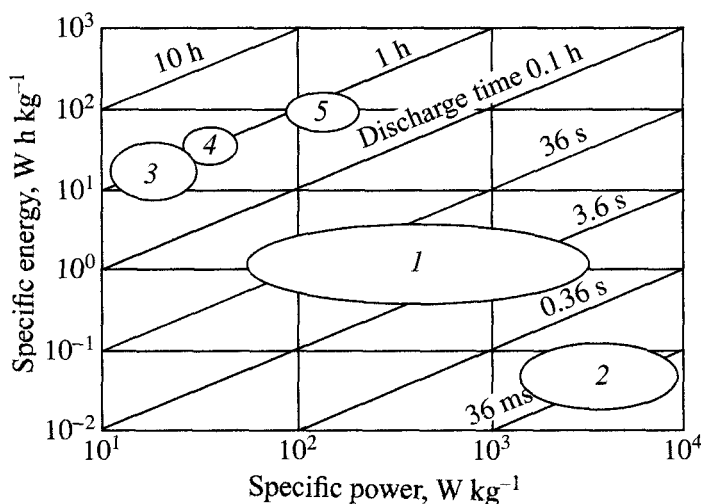


Figure 8.13. Comparison of the energy/power characteristics of selected batteries, conventional capacitors and supercapacitors. 1, supercapacitors; 2, electrolytic capacitors; 3, Pb-acid batteries; 4, Ni-Cd batteries; 5, lithium batteries. Typical discharge times are also indicated. (From Ref. 137)

the needs of demanding portable devices.

## 8.9. Types of Supercapacitors

Electrochemical capacitors store energy by charge separation. They are constructed much like a battery: a positive and a negative electrode, an electrolytic solution, and a separator. There are basically three types of supercapacitors (electrochemical capacitors), as described in the following.

### *Double-layer capacitors*

In this type of supercapacitor, the electrolyte ions are driven during charge towards electrodes of opposite polarity. In this way, at each electrode a double layer is created in which positive and negative charges face one another. A schematic is shown in Figure 8.14 [138]. The current collector of each electrode contacts high surface area, conductive carbon impregnated with an electrolyte. Taking as a reference the negative electrode, the negative charges received during charge by an external source (e.g. a battery) are balanced by the positive charges of the electrolyte cations. These latter, as shown by the

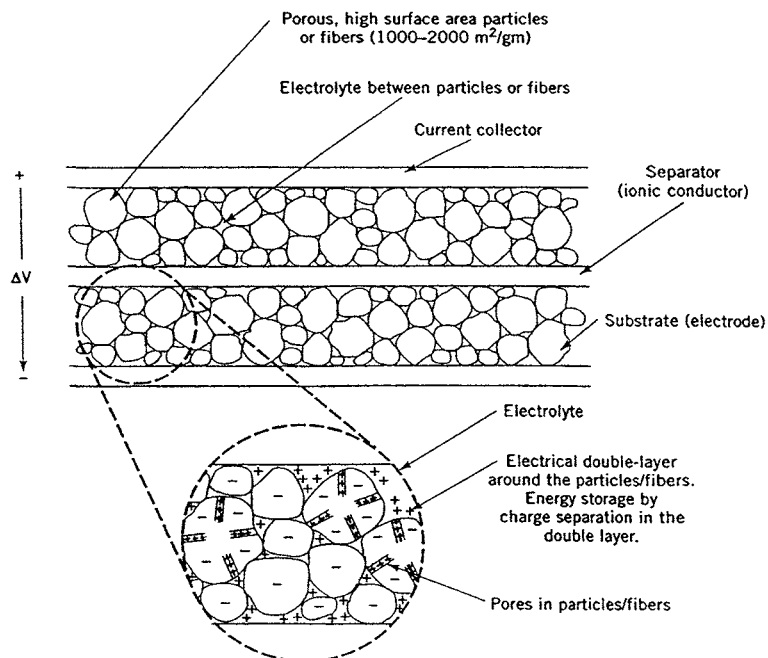


Figure 8.14. Scheme of a double-layer capacitor. (From Ref. 138)

magnified section of Figure 8.14, accumulate on the surface and within the micropores of the carbon particles. It can be said, because of the formation of a double layer at each electrode/electrolyte interface, that this latter represents a capacitor and the complete cell is formed by two capacitors in series [139]. The overall capacitance,  $C$ , is linked to the capacitances of the single electrodes by the relationship:

$$1/C = 1/C_+ + 1/C_-$$

In an ideal double-layer capacitor, only charge separation takes place at the electrodes and there are no oxidation or reduction (redox) reactions. With this assumption, the charge stored in the capacitor is related to its capacitance and voltage by the relationship:

$$Q = C \cdot V$$

The capacitance (Farad, F) of an electrode is voltage-independent and depends, instead, on the electrode surface ( $A$ ) and the double-layer thickness ( $d$ ):

$$C = K \cdot A/d$$

with  $K$  including the dielectric constant of the electrolyte solvent. The thickness of the double layer is in the order of 5-10 Å and its capacitance is 10-20  $\mu\text{F}/\text{cm}^2$  for a smooth electrode in a concentrated electrolyte [140]. Considering that in conventional capacitors the total capacitances are in the micro- to pico-farads range, exploiting the double layer to build capacitors with high capacity and energy has been a natural evolution in this field. Using porous carbon electrodes of high surface area allows obtaining high specific capacitances. For instance, with an electrode of 1000  $\text{m}^2/\text{g}$  and a double layer capacitance of 10  $\mu\text{F}/\text{cm}^2$ , the capacitance is 100 F/g. So, the capacitor will have a total capacitance  $C$  (see formula above) of 25 F/g of active mass. This supercapacitance, in turn, generates a high energy for the capacitor, according to the relation:

$$E = \frac{1}{2} C \cdot V^2$$

where  $V$  is the voltage between the capacitor plates; its maximum value depends on the type of electrolyte. With aqueous electrolytes,  $V_{\text{max}}$  is  $\sim 1$  V, this resulting in a maximum specific energy of  $\sim 3.5$  Wh/kg. With an organic electrolyte, a typical cell voltage is 2.3 V and the energy is  $\sim 18$  Wh/kg. These energy values are much lower than those of batteries, but well above those of



conventional capacitors (see also Figure 8.13). This means that the supercapacitor can deliver the power needed by the device for reasonably long times (up to several seconds).

The maximum power deliverable by the capacitor is given by:

$$W = V^2/4R$$

where  $V$  is the full-charge voltage and  $R$  is the equivalent series resistance (thus, also called ESR) which, in a double-layer capacitor, is just the sum of ionic and electronic resistances. Lowering  $R$  means having higher power.

One of the characteristics of a capacitor, often mentioned also in commercial products, is the so-called time constant  $\tau$ , *i.e.* the product  $RC$ . Capacitors with small time constants are those delivering high power in a relatively short time, while high constants are typical of capacitors that discharge relatively longer. Ideal applications for ECs are those asking for energy pulses of duration in the time range  $10^{-2} \leq \tau \leq 10^2$  seconds.

#### *Electrochemical capacitors with redox reactions*

In these ECs, a fast charge transfer occurs at the electrodes, and the so-called pseudo-capacitance arises [138]. The charge transferred in these redox reactions is voltage-dependent and so is the capacitance.

Two classes of materials are investigated for these pseudo-capacitance ECs: metal oxides and conducting polymers.

Ruthenium oxide,  $\text{RuO}_2$ , is the most investigated in the first class, both in the anhydrous and in the hydrated form. In aqueous acid electrolytes, the basic charge storage process is  $\text{H}^+$  insertion into the oxide structure. The resulting specific capacity is very high: 750 F/g [140].

Some polymers that can be positively or negatively doped by electrolyte ions form the second class. Positive doping (p-doping) and undoping is an easy process for such polymers as polypyrrole, polythiophene and polyaniline. The charge generated at each monomer unit is balanced by an anion as, for example,  $\text{BF}_4^-$ . These materials appear promising as they: can produce capacitances in excess of 200 F/g, have fast doping/undoping kinetics, high conductivity in the doped state, and relatively low cost [141]. Conversely, negative doping (n-doping) is not a smooth process and only polythiophene and some of its derivatives can be n-doped at potentials compatible with electrolyte and polymer stability. The long-term stability during cycling may still be a problem as the dopable polymers tend to swell and shrink, this causing degradation [140].

#### *Hybrid capacitors*

Supercapacitors can be assembled with one carbon (double-layer) electrode and a battery-like electrode. These ECs, referred to as hybrid

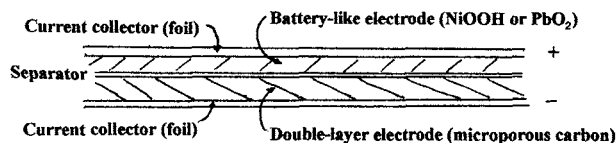


Figure 8.15. Schematic of a hybrid supercapacitor. (From Ref. 138)

capacitors, are built to combine the most favourable features of batteries (high energy) and ECs (high power). Their construction is depicted in Figure 8.15. At variance with those of double-layer ECs, their charge/discharge characteristics are non-ideal (non-linear).

Early hybrid ECs used electrodes typical of aqueous commercial batteries, *e.g.* NiOOH or PbO<sub>2</sub>. In recent years, however, intercalation electrodes, such as the oxides used in Li-ion batteries, have also been exploited (see later).

A hybrid EC can also be constructed with a double-layer electrode and a pseudo-capacitance electrode, such as polymethylthiophene. Laboratory prototypes of such a hybrid have shown a better performance in terms of energy and power with respect to double-layer ECs [142].

## 8.10. Characteristics of Available Supercapacitors

Most of the supercapacitors commercially available are of the double-layer type. Some hybrids have been proposed, *e.g.* with Ni oxide in an aqueous electrolyte [138] or with an intercalation material in organic electrolyte [143]. Some characteristics of double-layer and hybrid ECs will be here described.

The nature of the carbon electrode largely determines the specific capacitance of the EC. Carbon black, cloth, aerogel carbon, particulates from SiC or TiC, and carbon nanotubes have been proposed. In Table 8.3, the specific capacitances of selected C electrodes are reported. It can be noted that the capacitances in organic electrolytes are lower than those in aqueous electrolytes. This is explained by the fact that a large fraction of the carbon surface area is in pores, and the smallest pores cannot be accessed by the bulky ions and organic solvent molecules. A typical organic electrolyte is tetraethylammonium tetrafluoroborate (Et<sub>4</sub>NBF<sub>4</sub>) in propylene carbonate (PC). Porous carbons for supercapacitors should have pores of diameters 1-5 nm, as smaller pores produce remarkable capacitance decreases especially at high currents.

Table 8.3. Specific capacitances of carbon electrodes. (Adapted from Ref. 138)

Material	Density (g/cm <sup>3</sup> )	Electrolyte	F/g	F/cm <sup>3</sup>
Carbon cloth	0.35	KOH	200	70
		Organic	100	35
Carbon black	1.0	KOH	95	95
Aerogel carbon	0.6	KOH	140	84
Particulate from SiC	0.7	KOH	175	126
		Organic	100	72
Particulate from TiC	0.5	KOH	220	110
		Organic	120	60

Aerogel carbon is high surface area foam characterized by low ESR and high power and energy values. Small supercapacitors based on this carbon are commercially available for a number of applications [144]. ECs based on carbon nanotubes are in their development stage. The nanoscale dimensions of the particles could produce higher surface area and, hence, higher capacitance and energy. Japanese researchers foresee the possibility of reaching energy densities of 60 Wh/L with appropriate nanomaterials.

Examples of commercially available small supercapacitors are listed in Table 8.4. Most of these ECs use an organic electrolyte, this explaining the rated voltage of 3 V. The maximum capacitance (13.4 F/g for Superfarad) is some orders of magnitude larger than that of conventional capacitors used in electronic circuits. RC can be as low as 0.08 sec (Cap-XX), this resulting in a specific power approaching 2000 W/kg for 95% discharge efficiency. On

Table 8.4. Performance characteristics of selected small supercapacitors. (From Ref. 138)

Device	Voltage (V)	Capacity (F)	Resistance ( $\mu\Omega$ )	RC (s)	Wh/kg	W/kg <sup>1</sup> (95% eff.)	Weight (g)
Superfarad	1.4	114	20	2.3	2.5	324	8.5
Maxwell	3	10	100	1.0	1.75	444	6.6
PowerStor	3	2.5	40	0.1	0.57	1150	5.5
Cap-XX	3	120	26	3.1	5.8	374	26
Cap-XX	3	30	7.4	0.22	1.5	1368	25
Cap-XX	3	10	8.1	0.08	0.74	1838	17

1. Calculated with the equation:  $W=9/16(1-EF)V^2/R$ , where EF is the capacitor's discharge efficiency and V is the rated voltage.

the opposite end, high time constants result in higher specific energies, with a maximum of about 6 Wh/kg for Cap-XX's capacitor ( $RC = 3.1$ ). Just like in batteries, high powers can be achieved by using very thin electrodes (less than 0.1 mm), at the expenses of the ratio between active and inactive materials.

It has been calculated that there is room for improving the energy and power values of Table 8.4 with presently available carbon electrodes (especially cloths and foams), low-resistivity organic electrolytes and optimized cell design. Specific energies of 8-10 Wh/kg and maximum specific powers of 2-3 kW/kg seem a realistic goal [138]. Further improvements may come from the above-mentioned carbon nanotubes.

Hybrid ECs with a carbon electrode and NiOOH (in aqueous KOH) are also commercially available, but as large modules. Calculations based on the use of thin electrodes (10-125  $\mu\text{m}$ ) have shown that interesting energy and power values can be obtained. Similar calculations for a hybrid with a  $\text{PbO}_2$  electrode (in aqueous  $\text{H}_2\text{SO}_4$ ) give even better energy values (approaching 20 Wh/kg). Power densities of several kW/kg are expected. The main concern with these hybrids is their shelf and cycle life due to the presence of a battery-like electrode [138].

A hybrid based on carbon and an electrode capable of inserting  $\text{Li}^+$  in an organic electrolyte has recently been presented [143,145]. Its operation principle and a slim version are shown in Figure 8.16. In this EC, carbon is the positive electrode, while the negative is spinel-structured  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . During the

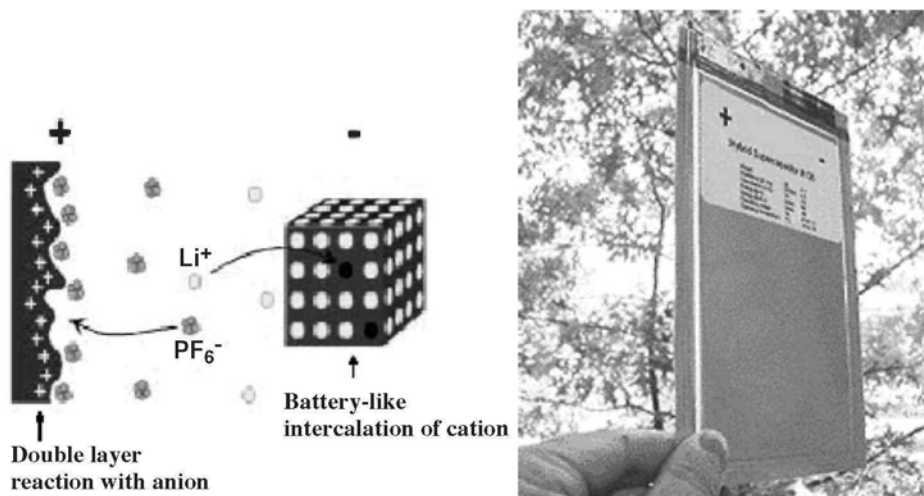


Figure 8.16. Principle of operation (during charge) of a hybrid supercapacitor with C and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  in non-aqueous electrolyte (left); example of the dimensions of this EC (right). (From Ref. 145)

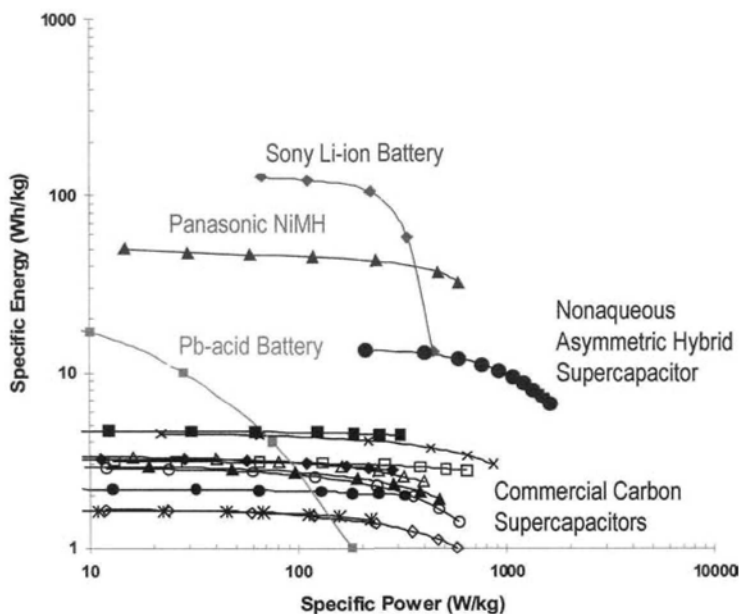


Figure 8.17. Ragone plot (W/kg vs. Wh/kg) for commercial double-layer ECs, some rechargeable batteries and a non-aqueous hybrid capacitor. (From Ref. 145)

EC's charge, anions from the salt reach the C electrode and form a double layer, while  $\text{Li}^+$  cations are inserted within the tunnels of the spinel structure. It is to be noted that the latter is used in the form of nanoparticles. A characteristic of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is its ability to reversibly insert  $\text{Li}^+$  without structural alterations that might lead in the long run to EC's degradation. A lifetime of more than 300000 cycles is reported and both electrodes are produced in commercial quantities. As can be noted in Figure 8.17, this non-aqueous hybrid capacitor can reach substantially higher energies in comparison with double-layer ECs, while maintaining a high specific power. Typical discharge times for this EC are 10 sec or more (see later for applications).

### 8.11. Advantages and Limitations in the Use of Supercapacitors

The advantages can be summarized as:

- Fast charging. ECs can be charged in seconds, while batteries require hours.

- No need of charge control. There are no overcharging problems (long overcharge times, however, shorten the EC's life).
- Extremely long cycle life. Up to  $10^5$ - $10^6$  cycles may be obtained vs.  $10^2$ - $10^3$  for batteries.
- Cycling efficiency in excess of 95%.
- High power.
- No maintenance.
- Absence of toxic materials and easy disposal.
- Wide temperature range. ECs can be used in a wider range than batteries, *e.g.* -40 to 85°C.
- Limited heat dissipation because of the low energy content.

Conversely, the following limitations have been observed:

- Low energy. The present values of 1-5 Wh/kg (see also table 8.4) are well below those of batteries (from ~30 Wh/kg for Pb-acid to ~200 Wh/kg for Li-ion batteries)
- High self-discharge rate. Especially with organic electrolytes, self-discharge may reduce the initial capacity by up to 50% in one month.
- Low voltage. In aqueous electrolytes, the maximum voltage is 1.2 V; in organic electrolytes, the maximum is ~3 V, but the linear discharge curve typical of an EC causes a rapid decrease.
- The preceding point entails the need of series connection for some applications. Voltage balancing is required for more than three ECs in series.
- Cost. It is presently higher than that of batteries (see later).

## 8.12. Applications of Supercapacitors

Commercial ECs are available in a number of sizes, with capacities ranging from less than 1 F to more than 100 F, and time constants from less than 1 sec to more than 10 sec. A selection of electrochemical capacitors, all based on carbon electrodes, is shown in Figure 8.18.

The present applications can be divided into three classes.

*Backup sources.* Most of the ECs on the market are used in consumer electronics as backup sources for memories and clocks (*e.g.* in computers). In these applications there is a primary source powering the device – a battery in portable applications. In any event causing disconnection or failure of the battery, the EC can take over and allow for data saving. In order to do this, the EC should be mounted in parallel to the battery and as close as possible to the load (Figure 8.19).

Backup applications may be rather different and may require quite low



Figure 8.18. Some commercial electrochemical capacitors. A toy equipped with an EC is also shown. (From Ref. 140)

or quite high currents and times. This is shown in Table 8.5, listing several applications, many of them relating to portable devices.

Large currents are delivered by low-ESR supercapacitors for times in the range: few milliseconds to 1-2 seconds. On the other extreme, high-ESR ECs can sustain  $\mu\text{A}$  currents for backup times of up to several days. This clearly indicates that ECs are not only short-time, high-power sources.

The backup function in popular portable devices as notebooks, cellular phones, PDAs, and photo- and video-cameras can be further stressed. Back-up in these devices is needed during battery replacement and may take seconds or minutes. Not only double-layer ECs, but also hybrid ECs (e.g. the non-aqueous ones with an insertion electrode [146]) may be used in this case.

*Main power source.* In these applications the EC delivers one or several pulses with durations in the msec-sec range and, afterwards, is recharged

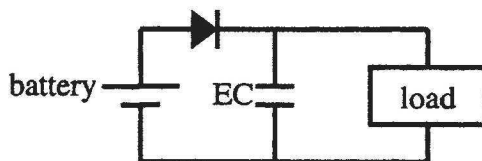


Figure 8.19. Battery-supercapacitor arrangement in an electronic circuit. The blocking diode prevents current flow from supercapacitor to battery. (From Ref. 140)

Table 8.5. Typical back-up applications of supercapacitors. (Courtesy of Tokin)

Functions	Backup Current	Applications	Equipment
Large current supply	Up to 1A	Actuator applications (Large current in a short period)	Actuators Relays / Solenoid Starters
		Primary power supply for LED displays, toys, electric buzzers, etc.	Handheld toys Displays, Smoke detectors, Alarm devices, Emergency displays
Medium capacity power supply	Up to 50 mA	Secondary power source for undesirable voltage drops	Vehicle radio back-up at engine start, etc.
		Motor start	VCRs, video disks, record players
Power backup for primary power outages	Less than 500 $\mu$ A	CMOS Microcomputers	Phones (Memory dial, Auto-answering) Electric cash registers, Electric typewriters Computer terminals Automatic measuring instruments, etc.
		CMOS RAMs ICs for clocks	Digital tuning audio systems LW-MW-FM Radio, Car Radio, Stereo, etc.) Programmable consumer electronic products (VCRs, Microwave ovens, Games, etc.)
		CMOS RAMs High operating temperature (85° C)	Measuring instruments, Automatic controls, Communications, Automotive

by a battery. Typical applications include the following [140]:

- Toys: for example the car of Figure 8.18. Charging takes few seconds and the EC can then power the car for several seconds.
- Fail-safe position: the EC can power an actuator to open or close positioning in case of power failure.

*Alternating power source.* The EC may complement the work of batteries, fuel cells or solar cells. The nice features mentioned above, *e.g.* long cyclability, large temperature range, high efficiency and high power (in most cases), make ECs ideal for these applications. For instance, in conjunction with a fuel cell, the EC can improve the dynamic response to load variations, which is a weak point of fuel cells, as commented in Section 8.4.

Appealing applications are those connected with the use of thin-type ECs in cellular phones, digital cameras and other electronic portable devices. A digital camera requires a current burst when zoom or flash are operated and the liquid crystal display is on. An EC can do the battery's job for these tasks. In Figure 8.20, thin ECs ideally suited for application in a camera are shown. It has been calculated that a 1.6 times longer battery life may be achieved in a camera endowed with a supercapacitor of this type. This feature allows the use of primary alkaline batteries in case of failure, or lack of power mains to recharge, of Ni-MH or Li-ion batteries.



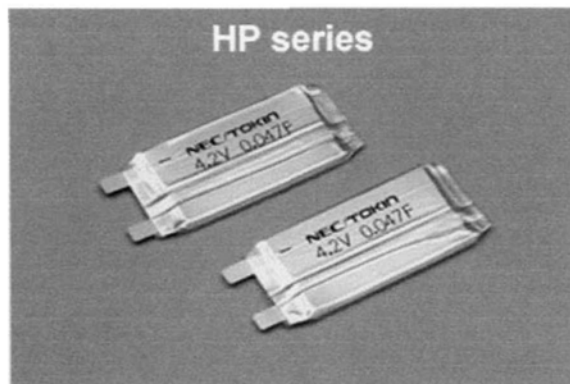


Figure 8.20. Thin-type supercapacitors for application in digital cameras and other electronic devices. 4.2 V, 0.047 F, max ESR 200 m $\Omega$ , dimensions: 29.5x12x2.3 mm (LxWxT). (From Ref. 146)

Other applications taking advantage of these thin ECs include the following: PDAs, wireless LAN, data communication cards, and external hard disk, CD or DVD drives for portable computers [146].

In GSM cellular phones, current pulses of 1.5-2 A for  $\sim 0.5$  msec are needed every  $\sim 5$  msec for transmission (see also Figure 5.55). The pulse power is about 10 times the average power. A battery/EC combination reduces the power output requested to the battery, as the EC delivers the largest part of the pulse, thus prolonging the battery life [140,147]. The time constant RC for an EC suitable for this application is below 1 sec. Some slim supercapacitors (less than 2 mm thick) are claimed to extend the effective talk time of cellular phones by more than 25%. These ECs can also be applied in RF modems: a version has been developed by Kyocera (AVX) that can fit into a PCMCIA card [148].

ECs can also be used in actuators, microsensors (see page 156) and in medical devices (e.g. defibrillators). Many more applications can be imagined, but it is to be stressed that ECs are not universal energy storage devices. Their ideal use is for power(W)/energy(Wh) ratios of  $\sim 10^3$ , as can also be inferred from Figure 8.13. Higher ratios are better managed by conventional capacitors and lower ratios by batteries.

Capacitors for electronic applications can be produced in large volumes and at relatively low costs. However, the EC's cost is presently higher than that of batteries. A 5-Wh/kg EC costs about 2.5 \$/Wh [149], while the cost of common secondary batteries is well below 1 \$/Wh (see, for instance, Table 5.1).

A list of ECs producers/developers is presented in Appendix G. Panasonic/Matsushita was the first to commercialize ECs in 1978, followed by

NEC/Tokin in 1980. Panasonic is by far the major producer [15]. Cooper/PowerStore, Maxwell, Ness, Kyocera/AVX, and Cap-XX are other distinguished companies in this field.

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## Chapter 9

# SPENT BATTERY COLLECTION AND RECYCLING

### 9.1. Introduction

In several countries, collecting batteries is becoming mandatory, and so is recycling those containing toxic materials. Recycling may also be applied to recovering valuable materials to be reutilized. A schematic representation of the steps constituting the ideal cycle of a battery is shown in Figure 9.1. A useful tool for determining the effectiveness of collection/recycling schemes is the so-called life cycle analysis (LCA) of batteries [151]. LCA is utilized to establish the relative environmental and human health impacts of battery systems over their entire lifetime, from the production of raw materials to the disposal of spent batteries. The three most important factors determining the total life cycle impact appear to be battery composition, battery performance, and the percentage of spent batteries recycled after their use. This analysis examines both rechargeable and non-rechargeable batteries.

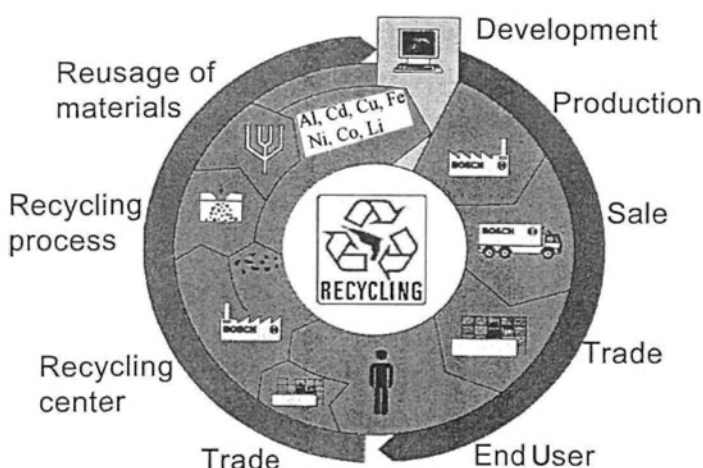


Figure 9.1. Schematic representation of a battery cycle from development to recovering of materials. (From Ref.150)

Battery elements such as lead, cadmium, mercury, nickel, cobalt, chromium, vanadium, phosphorus, lithium and chlorine, as well as acidic or alkaline electrolytes, may have adverse human health and environmental effects. In Table 9.1, the relative health impact of battery components is presented [152]. It may be surprising finding such elements as arsenic and antimony. In fact, these elements are present in the grids of some types of Pb-acid batteries. The health impact score of the table was calculated for the components of batteries to be used in electric vehicles. For this reason, a highly toxic element as mercury is not included in the list, as it is not used in the above batteries and can only be found in some Zn primary batteries at very low concentrations (see later).

The classification of Table 9.1 stresses that materials contained in Pb-acid and Ni-Cd batteries are highly dangerous for the human health and the environment. Some of the hazards for humans connected to cadmium and lead, as well as mercury, all dangerous heavy metals, are listed hereafter [153].

*Cadmium:* The acute (short-term) effects of cadmium in humans through inhalation exposure consist mainly of effects on the lung, such as pulmonary irritation. Chronic (long-term) inhalation or oral exposure to cadmium leads to a build-up of cadmium in the kidneys that can cause kidney disease. Animal studies have demonstrated an increase in lung cancer from long-term inhalation exposure to cadmium. The Environmental Protection Agency (EPA, U.S.A.) has classified cadmium as a probable human carcinogen.

*Lead:* Exposure to lead can occur from breathing contaminated workplace air or house dust or eating contaminated food. Lead is a very toxic element, causing a variety of effects at low dose levels. Brain and kidney damage, and gastrointestinal distress are seen from acute (short-term) exposure to high levels in humans. Chronic (long-term) exposure in humans results in effects on the blood, central nervous system (CNS), blood pressure, and kidneys. Children are particularly sensitive to the chronic effects of lead, with slowed cognitive development, reduced growth and other effects reported.

*Mercury:* The most important organic mercury compound, in terms of human exposure, is methyl mercury. Methyl mercury exposure occurs primarily through the diet, with fish and fish products as the dominant source. Acute exposure of humans to very high levels of methyl mercury results in CNS effects such as blindness and deafness. Chronic exposure to methyl mercury in humans also affects the CNS with symptoms such as blurred vision, malaise, speech difficulties, and constriction of the visual field.

Li-ion batteries also raise concern as cobalt (contained in the positive electrode,  $\text{LiCoO}_2$ ) and phosphorus (contained in the electrolyte salt,  $\text{LiPF}_6$ ) have high health and environmental impact [153]. Ni-MH batteries are dangerous as Ni is a suspected carcinogen [153]. Referring to the four most

Table 9.1. Relative health impact of major battery components. (From Ref. 152)

Material	Health Impact Score	Material	Health Impact Score
Arsenic	65	Fluorine	22
Cadmium	57	Zinc	21
Lead	56	Aluminum	20
Antimony	51	Carbon Black	20
Nickel	45	Vanadium	18
Cobalt	35	Tin	13
Manganese	33	Sulfuric acid	11
Phosphorus	33	Sulfur	9
Copper	31	Iron	8
Chromium	30	Zirconium	7
Lithium	25	KOH	5
Chlorine	23	Titanium	4
Sodium	23	Plastic	3

Note: A higher number indicates a greater effect

important rechargeable batteries, Pb-acid, Ni-Cd, Ni-MH and Li-ion, their composition and related classification in terms of health hazards is presented in Table 9.2. It can be noted that the majority of these components pose safety risks.

The degree to which batteries are collected and recycled after their useful life may largely mitigate their adverse effects. Landfill or incineration disposal options are not as desirable as recycling, but the risks associated with those options are not unacceptably high. At present, it appears as if improvement in the recycling rates of spent batteries will produce the most substantial decrease in the environmental and human health impact of battery systems.

In general, the following stages in the battery life are to be considered as contributing to human health and environmental impact [151]:

- Raw materials production
- Battery production process
- Distribution and transportation
- Battery use
- Recharging and maintenance (secondary batteries)
- Recycling or other waste management

Each of these stages requires energy and materials. As shown in Figure 9.2, the inputs of energy and materials on the left hand side for every stage in the manufacture, use and disposal of a battery are balanced by the outputs of usable products and environmental releases on the right hand side.

Table 9.2. Components of portable rechargeable batteries and their safety hazards. (From Ref. 154)

Battery Components	Pb-A wt%	Ni-Cd wt%	Ni-MH wt%	Li-Ion wt%	Classification
Cadmium	-	14-20	-	-	T toxic
Nickel	-	16-21	30-42	-	Xn harmful
La,Ce,Nd,Pr	-	-	8-10	-	-
Cobalt	-	0.4-0.6	3-4.5	16-18	Xn harmful
Iron	-	3 0-4 5	22-25	-	-
Electrolyte (KOH)	-	18-22	5-10	-	C corrosive Xi irritant
Aluminum	-	-	0.5-2	14-16	-
Copper	-	-	-	6-7	-
LiPF <sub>6</sub>	-	-	-	2-3	T toxic
Solvent (organic)	-	-	-	16-18	Xn harmful F flammable
Carbon	-	-	-	18-20	-
Lead	65-70	-	-	-	T toxic
Electrolyte (H <sub>2</sub> SO <sub>4</sub> )	22-30	-	-	-	C corrosive Xi irritant
Plastics, etc.	8	5	4	2-4	-

To produce the least impacts, the environmental releases from all of these stages should be minimized. Certain stages, such as the emissions associated with distribution and transportation, are insignificant. Also, sealed batteries have no emissions during normal use, while the emissions associated with the recharging of batteries depend very much upon the energy source: with clean energy sources, the emissions are virtually non-existent. Raw material production, battery manufacture, battery performance during use, and battery recycling or disposal are the most important stages. The emissions associated with each of these stages, and the corresponding energy consumed, will establish the impact of each battery system [151].

The battery impact must be expressed in terms of effects per kilowatt-hour of energy generated. This requirement is necessary since battery systems

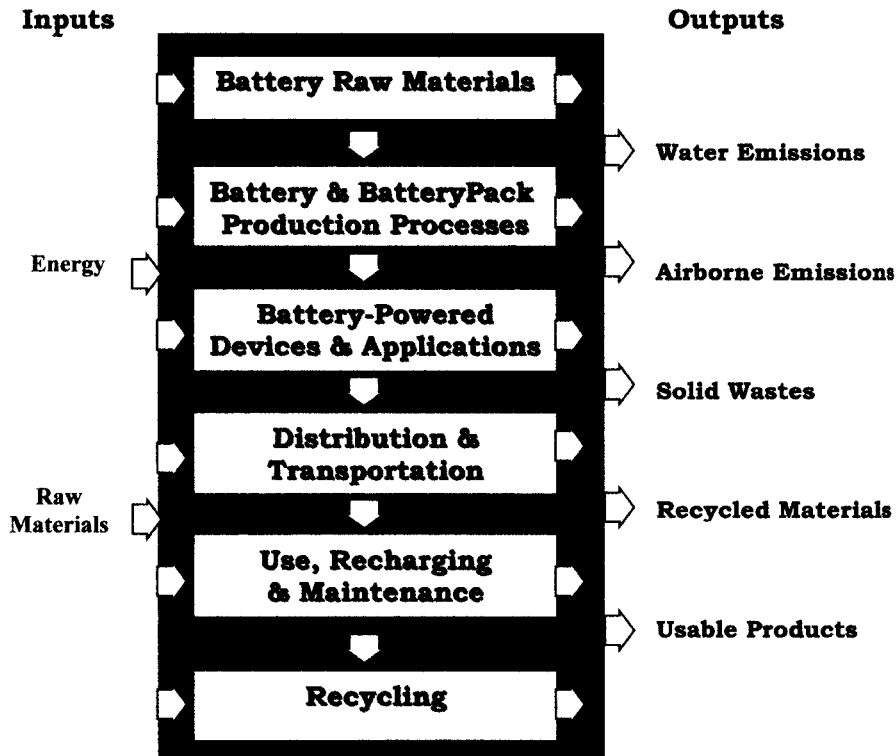


Figure 9.2. Materials and energy inventory analysis for battery systems. (From Ref. 151)

differ considerably in their total energy output. Rechargeable batteries have higher total energy outputs than non-rechargeable batteries, and thus their environmental and human health impacts are lower.

In a life cycle impact analysis of battery systems, it is clearly the final disposal of the battery which determines its major impact. The emissions associated with all the stages up to the disposal of the battery are perhaps only 1% to 2% of the total potential emissions if the battery is simply discarded into the environment. These figures change, of course, if the battery is disposed of in a controlled manner such that emissions are minimized. Nonetheless, disposal is the key step in determining total environmental or human health impact.

As hinted above, there are three possible options for the disposal of spent batteries –incineration, land filling or recycling. Incineration is not a preferred option: batteries do not burn well, and their mass is not substantially reduced. Therefore, batteries, which are invariably contained in municipal solid waste (MSW) streams, will become part of the residue from MSW incineration process. During this process, fine fly ash emissions occur and the filters should



capture more than 99% of them, but then the fly ash must generally be land filled.

The two most likely options for the disposal of spent batteries today are land filling and recycling. Land filling, currently the most widely used option, does not necessarily pose an immediate threat to human health and the environment. For example, a study made by the University of Berne in 1998 on landfill leachate data from landfills in Canada, Denmark, France, Germany, Italy, Japan and Switzerland indicated that the vast majority of leachate samples passed the World Health Organization's (WHO) recommended cadmium drinking water standard of 3  $\mu\text{g}$  per liter [155]. Some of the data included in this survey were obtained from 50-year old unlined landfills, which theoretically should represent a worst-case environmental impact scenario.

However, the most preferred option for the disposal of spent batteries is obviously collection and recycling. This option greatly reduces any risk that may exist and conserves valuable natural resources. Lead-acid batteries have already achieved impressive recycling rates, better than 90% in the United States, and growing rates are reported all over the world. For Ni-Cd batteries, the issues are: how to improve collection rates, how to finance collection and recycling programs to improve returns, how to label batteries to maximize collection, and how to measure recycling rates. With Ni-MH and Li-ion batteries, the main issue is improving the recycling technologies to maximize materials recovery. With the alkaline manganese and carbon zinc batteries, the main point is the economics of the collection and recovery processes.

Obviously, collection and recycling of a spent battery prevents the entry of the majority, probably greater than 98%, of the battery's weight into the environment after use. However, the relative energies required to recycle various battery systems must also be considered. Nickel-cadmium and lead-acid batteries are relatively easy to recycle because the reduction of nickel, iron, cadmium and lead oxides to pure metals requires less energy than the reduction of the oxides of other battery metals (such as zinc, manganese, titanium, zirconium and lithium), which are constituents of alkaline manganese, Ni-MH and Li-ion batteries.

Once an assessment is made of the emissions of a battery during its life cycle, the impact of these emissions has to be evaluated. It is unfortunate that there is not a unique evaluation method, but some methods based on different approaches and, so, often providing contradictory results. Details about this matter are outside the scope of this chapter, but it can be stressed that mercury, lead and cadmium are consistently listed as the metals with the highest impact. However, it can be noted that nickel, cobalt, zinc and chromium are also listed as materials of concern by some evaluation methods [151].

To complete this introduction section, a table presenting the heavy metal content of batteries for portable applications may be useful. Table 9.3 lists common household batteries found in a typical municipal waste stream.

The Zn/HgO battery has been banned several years ago, because of its high mercury content, but it is not unlikely to find some old batteries discarded. Present manufacturing of Zn-C and alkaline batteries does not use any mercury, but small percentage may be found in the old ones or in those produced in countries with less restrictive regulations. Zn/Ag<sub>2</sub>O and Zn/air button cells may still contain up to 1% Hg.

## 9.2. Where do Spent Portable Batteries Go?

In the preceding section, it was shown that spent batteries are either separately collected or released into the MWS. The question, especially important for the small batteries powering portable devices, is: how many batteries, as a percentage of those used by consumers, can be collected in authorized collection sites or found in the MWS?

A number of primary and secondary batteries are used by a typical

Table 9.3. Types of batteries found in a municipal solid waste stream. (From Ref. 156)

Battery types and sizes	Typical heavy metal weight per cell
Alkaline (9 volt, D, C, AA, AAA)	Mercury: 0.025% or none
Carbon-zinc (9 volt, D, C, AA, AAA)	Mercury: 0.010% or none
Mercuric oxide* (button)	Mercury: 35-50%
Silver oxide (button)	Mercury: 0.4-1.0%
Zinc-air (button)	Mercury: 0.4-1.0%
Lithium (9 volt, C, AA, coin, button)	N/A
Nickel-cadmium (9 volt, C, D, AA, AAA, battery packs)	Cadmium: 10-15%
Small sealed lead-acid (pack configurations)	Lead: 50-75%

\*No longer produced

consumer. Some of them get exhausted relatively frequently, *e.g.* the primaries used in a radio or a walkman, and are either brought to a collection center or just thrown into the dustbin. Others, especially the rechargeable ones used, *e.g.*, in cameras or portable computers, last several years. It is conceivable that, once the device becomes obsolete, the battery remains within it. Such an obsolete device has one of these fates: a) is discarded; b) is brought back to a dealer; c) is kept home. In case a), device and battery enter the waste stream; in case b), a separate collection is made; in case c), the battery contributes to the “hoarding” phenomenon (home storage). In other words, considerable amounts of small batteries, especially the rechargeable ones, escape for long time any recovery.

The extension of the hoarding phenomenon can be understood looking at Figure 9.3, where data from an investigation carried out in Europe are represented. About 75% of the household batteries are hoarded, while the remaining 25% is collected by one of these three means: industrial waste, MSW, national or private collection scheme (NCRA = National Collection and Recycling Associations).

Hoarding has two major implications: a) the number of batteries collected is quite low with respect to those sold, this resulting in unrealistic collection rates; b) some hoarded batteries may become old with respect to new regulations, *i.e.* they may contain substances no longer permitted. The last issue is particularly significant if the user, after hoarding, throws the battery into the MSW. In this case, it is very likely that the battery will be land filled or

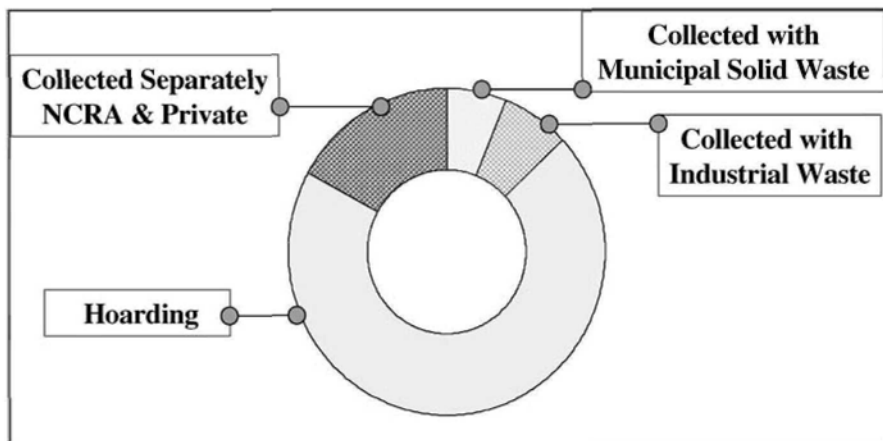


Figure 9.3. Hoarding vs. collection of portable rechargeable batteries. (From Ref. 157)

incinerated, procedures not recommended as stated in the previous section.

Campaigns to improve the contribution of the end user to the correct disposal of this type of batteries are in operation in several countries. An example is provided by the program *Charge up to Recycle!* of the Rechargeable Battery Recycling Corporation (RBRC, U.S.A.) [158]. Small rechargeable batteries, Ni-Cd, Ni-MH, Li-ion and Pb-acid, are collected in retail stores and community solid waste centers. Manufacturers support the recycling program by placing the RBRC's seal on rechargeable batteries and portable electronic products. The seal lets consumer know that the battery can be recycled. Another program is the *Big Green Box* that offers companies, municipalities and consumers in the U.S.A. a low cost and easy way to dispose correctly of their spent batteries and obsolete portable electronic devices. These can be stuffed in a pre-labeled container and sent to the recycling facilities without additional costs [159].

Other manufacturers in the most developed countries give their contribution to collection programs for portable batteries: in Europe, the European Portable Battery Association (EPBA) and CollectNiCad, the association taking specific care of Ni-Cd batteries; in Japan, the Battery Association of Japan (BAJ).

### 9.3. Collection and Sorting of Spent Batteries

When batteries for portable devices are collected, no initial attempt is made to distinguish them by size or chemistry. Therefore, the box in a collection point may contain a mixture of batteries like the ones shown in Figure 9.4. One ton of mixed batteries can contain up to 40000 individual battery units of 10 different chemistries [160]. The batteries can vary in size from button cells with a diameter less than 7 mm, and weighing less than 0.3 grams, up to packs weighing 1 kg or more.

Some simple safety rules have to be applied to battery collection. In particular, health hazards may be caused by: 1) large cell stocks, if not contained in plastic bags; 2) use of metallic containers, which may give rise to short circuits; 3) uncontrolled ambient conditions, *e.g.* heat, humidity, presence of other toxic substances; 4) including deteriorated batteries, *e.g.* with a corroded case; 5) not relying on properly trained personnel.

Non-differentiated spent batteries need some degree of sorting before being sent to the recycling facility. As will be later pointed out, there are cases, *e.g.* batteries from electronic waste, in which the sorting step can be skipped. Hand sorting of batteries is likely to be inaccurate and very time consuming



*Figure 9.4. A collection box with unseparated portable batteries. (From Ref. 160)*

even on a small scale. Consequently, automated battery sorting technologies have been developed.

Accurate sorting relies on the identification of a number of different properties of a battery. These include the physical size and shape, the weight, the electromagnetic properties and any surface identifiers such as color or unique markings [161]. These properties can be analysed in a number of different combinations in order to sort batteries according to their chemistry. It is now even possible to further separate the alkaline and zinc carbon cells into mercury-free and mercury-containing streams.

High speed and low cost are essential requirements of the operations carried out at the sorting facility. This means that large-scale facilities, in the order of 2000-3000 tons per shift, are preferred to smaller, more costly operations. Such facilities can be operated at a cost not exceeding \$150 per ton. One example is provided by the Sortbat sorting facility, operated in Rotterdam, The Netherlands, for separating primary batteries before their recycling. The heart of this sorting line is an electromagnetic sensor which induces a magnetic

field within each battery and measures either a voltage or a frequency response. Each battery is presented to the sensor by conveying it on two parallel belts, and transported directly through the centre of the sensor coils. This transport method allows each battery to pass through the sensor in a very stable manner, thereby ensuring the accuracy of selection. The signal from the sensor is stored electronically and processed together with an accurate weight measurement. It is this combination of electromagnetic sensing and weighing which is responsible for the high purity levels achieved. Both measurements are carried out without the need to stop the battery: the operation is carried out at high speed. Today, a sensor is capable of measuring five cells every second, and this speed will probably be doubled in the future.

*Table 9.4.* Different fractions obtained by the sorting of a battery mixture in a recycling plant using X-ray sensors. (From Ref. 162)

	<b>Output fractions</b>
1	Alkaline manganese batteries (UV marked, Hg < 5 ppm)
2	Alkaline manganese military batteries (Hg > 1000 ppm)
3	Alkaline manganese batteries (not UV marked, Hg < 200 ppm)
4	Zinc-carbon batteries (UV marked, 4R25 cells, 0 % Hg labeled, < 5 ppm)
5	Zinc-carbon batteries (not UV marked, Hg < 100 ppm)
6	Zinc-air batteries (electric fence energizer batteries)
7	Nickel-cadmium accumulators
8	Nickel-metal hydride accumulators
9	Lead-acid accumulators (small cells)
10	Lithium batteries
11	Lithium-ion accumulators
12	Button cell mixtures and mercury oxide round cells
13	Non-sortable battery mixtures
14	Household waste, electronic waste, capacitors, alkaline waste water

The sorting installation is also endowed with an ultra violet (UV) detector: this allows detecting an UV marker on the label of mercury-free batteries. In this way, they can be separated from those still containing Hg, and sent to recycling facilities where less Hg-tolerant processes are used.

X-ray transmission technology can also be used in a sorting line, as it can provide information for battery recognition and classification. Different batteries give different x-ray images and can be separated [162,163]. The X-ray sensor is able to identify up to 50 batteries per second. However, battery feeding and ejection are rate-determining steps, so that the average sorting rate is 15 batteries per second. For AAA and AA cells, this means a sorting of 50000 batteries per hour. In the SORBAREC plant of Bremerhaven, Germany, 13 battery output fractions can be obtained, as reported in Table 9.4

The separation afforded by these automatic processes is quite good and the sorted fractions have a minimum, if any, contamination level [162].

## 9.4. Battery Recycling

### 9.4.1. Aqueous Primary Batteries

It has been calculated that 80% of all primary batteries sold are either Zn-C or alkaline batteries. By mid-1990s, all major manufacturers eliminated Hg from these batteries, so that their proper disposal does not pose a health or environmental risk. In the U.S.A., E.U. and Japan, these batteries are not regulated as hazardous or dangerous wastes [164]. However, in the interest of resource conservation, the battery industry has developed recycling technologies for aqueous primary batteries that are safe, cost effective and with no impact on the environment. Only the basics of these processes will be here mentioned.

*Hydrometallurgical processes.* These processes differ from pyrometallurgical approaches in that they aim to produce finished products with a high resale value rather than lower value materials to be further refined or used in a separate industry [161]. Zinc/air batteries are often treated together with the alkaline and zinc carbon ones.

In a typical process, the batteries are sorted and shredded. The alkaline and zinc carbon batteries are shredded in an automated unit, the former under NaOH and the latter under a water spray. The water wash is necessary to eliminate the chlorides within the Zn-C cells before leaching.

The fraction consisting mainly of zinc, manganese oxides and carbon is leached in a NaOH bath. This selectively dissolves the zinc. Any amalgamated mercury present in the zinc precipitates out at this time and settles at the bottom of the reactor. After filtration, the zinc-rich filtrate is allowed to cool naturally,

and then dendritic zinc is deposited by electrolysis. This is potentially a high value material used within the paint industry.

The treatment of zinc-air batteries is somewhat simpler because of the absence of manganese dioxide. After the batteries have been opened, they are immersed in a NaOH bath. Zinc powder, zinc oxide, carbon and lime are dissolved/suspended in solution and undergo the same zinc treatment as described above.

*Pyrometallurgical processes.* One example is the pyrometallurgical process developed by Sumitomo Industries in Japan. The first stage is a thermal treatment at 400-750°C to eliminate organic substances and mercury: the organics are destroyed by burning, while the liberated mercury is further distilled and sold.

The thermal treatment is followed by smelting of the metallic fractions in a furnace. The batteries are automatically fed into the furnace, a reductant is added and the iron and manganese are melted to produce ferromanganese while the zinc evaporates. The liberated zinc then passes through a splash condenser where solid zinc is recovered [161].

*Electric Arc Furnace (EAF).* With the elimination of Hg from all primary consumer batteries, a less complex recycling route became available. Today, alkaline and Zn-carbon batteries can be successfully recycled within the existing metals industry.

The main area of interest for recycling spent primary batteries is the steel-making electric arc furnace. The Hg-free Zn-C and alkaline batteries have very good synergy with typical feeds used in the existing EAF's recycling process. The steel, manganese, carbon and zinc, which constitute in the order of 65% of the batteries by weight, are all successfully recycled or reused within this process.

#### **9.4.2. Nickel-Cadmium and Nickel-Metal Hydride Batteries**

Recycling of Ni-Cd batteries is done with a thermal process. More precisely, 90% of the batteries and wastes from the production of Ni-Cd batteries are treated with the closed furnace process [160]. The products to be treated are put into a vessel placed in a chamber that is closed and sealed with the exception of an outlet for:

- the gases produced by the decomposition of organic materials, vaporization of water and decomposition of hydroxides or oxides;
- the gaseous cadmium which has to be cooled to become liquid and then solid in either a confined space or in water.



The purity of the cadmium obtained is quite high, but it usually needs to be further refined to a purity of 99.99%, the only readily marketable quality for, among other things, the production of nickel-cadmium batteries.

The constantly increasing use of sealed cells that cannot be disassembled and which contain organic materials has meant the introduction of two pre-treatments:

- Removal of the plastic casing. The shell can be broken and separated from the individual Ni-Cd elements by means of, for example, a magnetic separator.
- Pyrolysis or oxidation of the elements (or possibly of the power pack as is). Pyrolysis is done in a sealed furnace. The organic materials are broken down into short organic chains at a temperature below those of cadmium distillation or cadmium oxide sublimation.

A scheme of the Ni-Cd battery recycling process is shown in Figure 9.5. It depicts the sequence of operations carried out at the recycling plant of SNAM, France, which has a capacity of 6000 tons of batteries per year [160].

Recycling of Ni-MH batteries is also made by a thermal process. It aims at recovering nickel and the small amount of cobalt also present (see Table 9.2), according to the scheme of Figure 9.6.

### **9.4.3. Lithium and Lithium-Ion Batteries**

In the recent past, most lithium batteries were either put into a landfill or incinerated. However, many of the larger lithium primary systems were so reactive that open detonation was used as an effective disposal method. Nowadays, in several countries, Li and Li-ion batteries are collected and recycled. The reactivity of batteries containing Li as a negative electrode is obviously different from that of the Li-free Li-ion batteries. Several companies are now developing recycling processes devoted to the latter battery type.

However, a recycling process for all Li and Li-ion batteries, regardless of size or type, has been in operation in the last several years. The essence of the process, developed by Toxco (Southern California, U.S.A.), is the lowering of the reactivity by reducing the temperature of the batteries [165]. Typical chemical reaction rates are halved for every 10°C drop in temperature. Placing the batteries in liquid argon or liquid nitrogen reduces the reactivity to less than  $1/250\,000^{\text{th}}$  of their room temperature reactivity. At these temperatures, the batteries are close to inert and can be safely handled regardless of their specific chemistry. Once frozen, the batteries are mechanically reduced in size by shearing, cutting or shredding. After recovering the metals, an alkaline solution is added to the electrodes/electrolytes mix to obtain inert compounds. The soluble components, including virtually all the lithium, are then processed

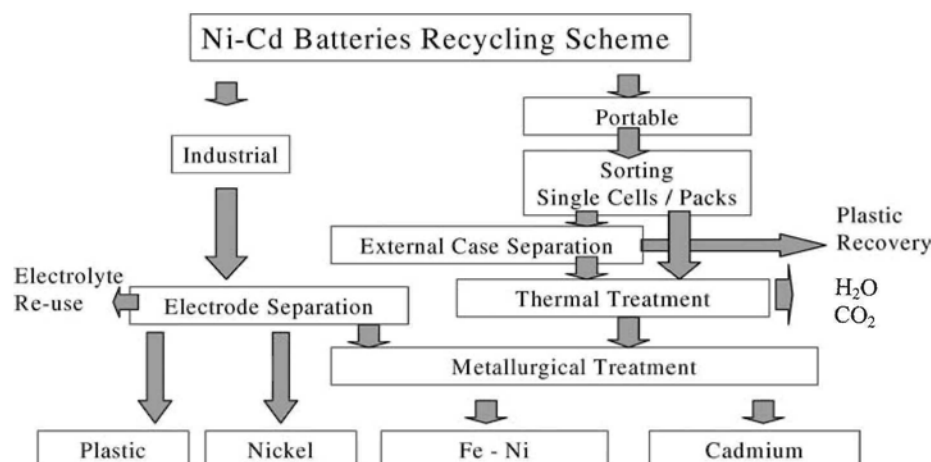


Figure 9.5. Nickel-Cadmium battery recycling scheme at SNAM (France). (From Ref. 160)

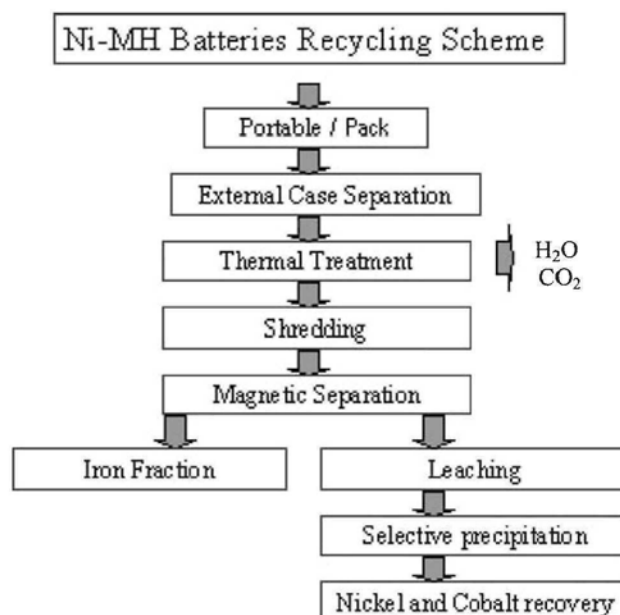


Figure 9.6. Nickel-Metal hydride battery recycling scheme at SNAM (France). (From Ref. 160)

through a series of wet chemistry baths and filters to yield  $\text{Li}_2\text{CO}_3$ , which is a basic building block compound for the lithium industry.

Toxco has also developed a wet chemistry process dedicated to Li-ion batteries. Here, the batteries are shredded at room temperature (but large and still charged batteries are either discharged or cryogenically processed) and treated with an alkaline solution. Li is recovered as above, while cobalt is recovered as a cobalt/carbon cake (rich in cobalt). The total quantity of batteries recycled is about 1000 tons/year (2004).

Other recycling processes dedicated to Li-ion batteries include the following.

The Sony-Sumitomo process (Japan) incinerates the batteries, at less than 1000°C, with the aim of recovering chiefly cobalt, present in the positive electrode of these batteries at percentages of 15-20%. Co is recovered as  $\text{CoCl}_2$ , while scraps of less precious metal, as Fe, Cu and Al are also recovered [166].

The process described, for instance, by SNAM (France) [167] and KIGAM (Korea) [168] is essentially a mechanical/chemical one. The KIGAM's scheme is shown in Figure 9.7. It consists of two sections: the first is a physical process separating electrode materials, while the second is a chemical process intended to maximize Co and Li recovery. These two elements are separated in the leaching solution by precipitation of Co as a hydroxide. Cu/Al and Ni/Fe are also recovered.

The AEA Technology's process (UK) is based on a different approach and carried out at ambient temperature [169]. In principle, this technique allows recovering of the electrolyte, another precious component of Li-ion batteries. For this purpose, the batteries are shredded in an inert, dry atmosphere and the electrolyte is extracted by a suitable solvent, which is then evaporated. The electrodes, carbon and  $\text{LiCoO}_2$  are dispersed in a solvent and separated from other components by filtering. Finally, C and  $\text{LiCoO}_2$  are separated from one another by electrolysis in a LiOH solution:  $\text{Co}^{\text{III}}$  in  $\text{LiCoO}_2$  is reduced to  $\text{Co}^{\text{II}}$  in  $\text{CoO}$ .

#### **9.4.4. Lead-Acid Batteries**

Collection and recycling of Pb-acid batteries is a well established process that allows recovering of automotive and industrial batteries at very high rates. The small sealed batteries described in Chapter 5 are added to the stream of the large ones and treated in the same way.

The current recycling technology used world-wide involves various steps [170]:

- physical treatment;
- smelting/reduction of lead-bearing products;
- refining the lead obtained by smelting to meet the market specifications;

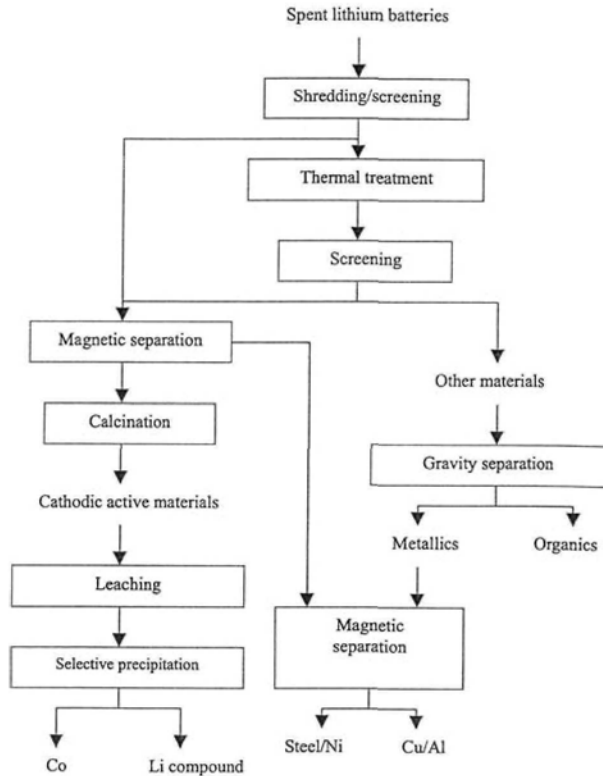


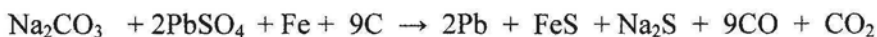
Figure 9.7. A recycling scheme of Li-ion batteries. (From Ref. 168)

- alloying.

The first operation requires the non-metallic components to be separated from the metallic fraction by crushing and physical sorting. In this way, reusable organic components are recovered.

Smelting is the key process in the cycle of spent lead batteries recovery. The lead paste can receive a carbonation before smelting or this can be made in the furnace by adding  $\text{Na}_2\text{CO}_3$ . This reaction has the advantage of transforming  $\text{PbSO}_4$  into  $\text{PbCO}_3$ , minimizing  $\text{SO}_x$  emissions and eliminating the need of special scrubbers. Carbon and scrap-iron are also added to the furnace.

If carbonation is made in the furnace, at  $1000^\circ\text{C}$  or below, the overall reaction is:



The yield in terms of lead is about 90%. Fe and  $\text{Na}_2\text{CO}_3$  prevent the

formation of  $\text{SO}_2$  (sulphides are formed). The metallic lead so obtained has to be electrolytically or thermally refined to obtain 99.9% grade lead. If required, a final alloying step is carried out, where high-purity alloys, such as Pb/Ca, Pb/Sb and Pb/Sn are produced.

#### 9.4.5. Batteries from Electronic Waste

Electronics is particularly prone to obsolescence and is creating the so-called electronic waste (or just e-waste). A couple of estimates carried out in the U.S.A. can provide the extension of this phenomenon: 130 million cellular phones are discarded annually; in the decade 1997-2007, 500 million computers have, or will, become obsolete.

As already mentioned, programs have started in the last few years to recover discarded electronic devices, such as those mentioned above, together with their batteries. These latter are, now, mostly Li-ion or Ni-MH, while some Ni-Cd and primary alkaline can also be present. In addition to the processes described in the previous sub-sections to recycle batteries sorted according to

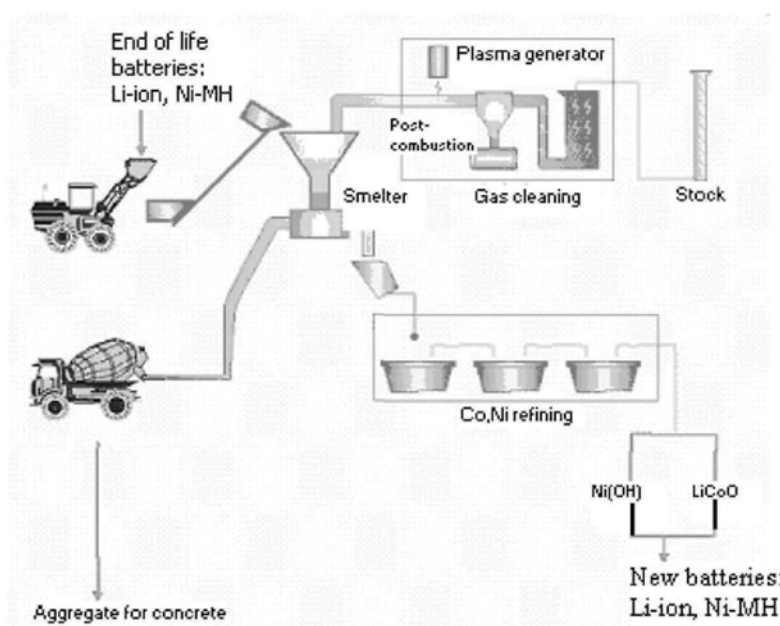


Figure 9.8. Umicore's process for recycling batteries from electronic waste. (From Ref. 171)

their chemistry, it is possible to treat such batteries without preliminary sorting. Here, the process developed by Umicore (Belgium) is described [171,172].

First, the batteries are separated from the electronic devices. These latter are recycled to recover metals, plastics, ceramics and glass. In addition to Li-ion and Ni-MH batteries, the specific recycling process shown in Figure 9.8 can tolerate a content of up to 10% of other batteries.

The spent batteries are sent to a smelting furnace, kept at the temperature of 1450°C, which can treat ~300 kg/h. Smelting produces an alloy containing all metals (*e.g.* Ni, Co, Cu, Fe) and a slag containing  $\text{Al}_2\text{O}_3$ , CaO and  $\text{SiO}_2$ . The two latter oxides are present because  $\text{CaCO}_3$  and  $\text{SiO}_2$  are added in order to have the alloy fluid at 1450°C. Volatile products from the smelter are properly treated to avoid pollution, while the slag is used in construction and/or aggregate for concrete, and plastics are valorized as a fuel. The carbon from Li-ion batteries is used in the furnace as a reductant. Ni and Co are subsequently treated to produce  $\text{Ni}(\text{OH})_2$  and  $\text{LiCoO}_2$  for new Ni-MH and Li-ion batteries, respectively. Up to 2000 tons of batteries per year can be treated and recycling rates above 90% for Li-ion and 80% for Ni-MH batteries are obtained.

## 9.5. Regulatory Issues for Battery Disposal and Recycling in the U.S.A. and E.U.

In this section, the rules set in the European Union and in the U.S.A. for the treatment of spent batteries will be briefly reviewed.

*E.U.* The E.U. produces more than 1 million tons of batteries a year (as of 2004), with portable (household) batteries amounting to about 160000 tons. In 2002, 45% of the household batteries sold to consumers ended up in the waste stream, in incinerators or landfill sites. Only 17% of them were collected after use.

The matter is still regulated by the European Council Directive issued in 1991 (91/57/EEC) and by the Directives of 1993 and 1998 adapting the first one to technical progress. In summary, these Directives cover batteries and accumulators containing certain (but not all) types of metals. In particular, “Member States shall prohibit, as from 1 January 2000 at the latest, the marketing of batteries and accumulators, containing more than 0.0005% of mercury by weight...Button cells and batteries composed of button cells with a mercury content of no more than 2% by weight shall be exempted from this prohibition”. It is mandatory the separate disposal of:

“1. Batteries and accumulators put on the market as from 1 January 1999 containing more than 0.0005% of mercury by weight.

2. Batteries and accumulators put on the market as from 18 September 1992 and containing:

- more than 25 mg of mercury per cell, except alkaline manganese batteries
- more than 0.025% of cadmium by weight
- more than 0.4% of lead by weight.

3. Alkaline manganese batteries containing more than 0.025% of mercury by weight placed on the market as from 18 September 1992”.

In November 2003, the European Commission has presented a new Directive with, basically, the following measures [173]:

- to ban the land filling or incineration of all automotive and industrial batteries;
- to set up national collection systems, allowing consumers to return their spent batteries free of charge;
- to set a collection target for consumer batteries of 160 g per inhabitant per year (corresponding to 4-5 portable batteries per person per year);
- to set a collection target of 80% for nickel-cadmium consumer batteries;
- to set recycling targets of 65% by weight for lead-acid batteries (all lead to be recovered), 75% for nickel-cadmium batteries (all cadmium to be recovered) and 55% for all other batteries;
- producers to be made responsible for costs related to collection, treatment and recycling;
- producers to be allowed to use a 'visible fee' for a maximum of five years after implementation.

In practice, all batteries should be collected and recycled to avoid pollution and to conserve resources. A maximum of 10% of the portable batteries collected is exempted from recycling (to account for damaged batteries).

On April 2004, the European Parliament has voted several amendments to this proposal, the most important being:

- a ban on all batteries or accumulators containing more than 5 parts per million (ppm) of mercury by weight, 40 ppm of lead, and/or 20 ppm of cadmium. A list of exemptions will be provided for applications where the use of these heavy metals is unavoidable - in other words, where no substitutes exist (including cordless power tools, aeroplanes and trains).
- a collection rate of 50% of the national annual sales of portable batteries instead of a figure of 160 g per inhabitant per year as proposed by the Commission, which would in practice have meant a collection rate of 40%.

The European Commission, on the other hand, stands firm on its original proposal and will reject many of the amendments. A second reading of the modified Directive is expected towards the end of 2004.

*U.S.A.* The matter in the U.S.A. is regulated by “The Mercury-Containing and Rechargeable Battery Management Act” (“The Battery Act”), issued in May 1996. The act states that: “(1) it is in the public interest to: (A) phase out the use of mercury in batteries and provide for the efficient and cost-effective collection and recycling or proper disposal of used nickel-cadmium batteries, small sealed lead-acid batteries, and other regulated batteries; and (B) educate the public concerning the collection, recycling, and proper disposal of such batteries; (2) uniform national labelling requirements for regulated batteries, rechargeable consumer products, and product packaging will significantly benefit programs for regulated battery collection and recycling or proper disposal; and (3) it is in the public interest to encourage persons who use rechargeable batteries to participate in collection for recycling of used nickel-cadmium, small sealed lead-acid, and other regulated batteries”.

Another important point is the labelling of batteries and products containing batteries: “Labelling. Each regulated battery or rechargeable consumer product without an easily removable battery...shall bear the following labels: (1) 3 chasing arrows or a comparable recycling symbol. (2)(A) On each regulated battery which is a nickel-cadmium battery, the chemical name or the abbreviation “Ni-Cd” and the phrase “BATTERY MUST BE RECYCLED OR DISPOSED OF PROPERLY”. (B) On each regulated battery which is a lead-acid battery, Pb” or the words “LEAD”, “RETURN”, and “RECYCLE” and if the regulated battery is sealed, the phrase “BATTERY MUST BE RECYCLED”.”

The final part of the Battery Act is devoted to Zinc-carbon and alkaline batteries: “No person shall sell...any zinc-carbon or alkaline-manganese battery manufactured with a mercury content ...except that the limitation on mercury content in alkaline-manganese button cells shall be 25 milligrams of mercury per button cell.” Obviously, Zn-HgO batteries were banned by this Act.

Like in the European Union, the legislation in the U.S.A. is now introducing the compulsory collection of all types of batteries. The state of California has enacted, in January 2004, the Universal Waste Rule. Under this rule, any company or public administration generating more than 10 kg per month of battery waste must either dispose of it in permitted facilities or recycle it. In 2006, consumers too will have this obligation. Other states are expected to follow California’s example.

To conclude this section, it can be pointed out that on April 2001, the “Law to Promote the Efficient Usage of Resources” was enacted in Japan. Under this law, manufacturers of portable rechargeable batteries (Ni-Cd, Ni-MH, Li-ion and Pb-acid), are required to collect and recycle used batteries.



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## Chapter 10

# WORLD BATTERY MARKET

### 10.1 General Trends

In the preceding chapters, the expansion of the battery market in the last several years has been mentioned. However, from 1998 to 2003, there was a moderate increase in the market in terms of total battery sales. Indeed, in the above period, the sales of primary batteries have arisen from 11 to 13 billion dollars and those of secondary batteries from 24 to 27 (the dollar value in the year 2000 was used) [15]. Part of these increments may only be apparent, as the US dollar has lately declined vs. euro and Asian currencies. On the other hand, the cost of some batteries, *e.g.* the Li-ion ones, has been decreasing.

Primary Zn/MnO<sub>2</sub> and Pb-acid batteries for starting, lighting and ignition (SLI) account for ~80% of the battery market by value. All primary batteries (including Li and other Zn-based batteries) amount to ~35% in terms of value. This corresponds to 80% in terms of number of primary batteries over the total of batteries sold. The sales of primaries have continued to increase in recent years, while those of Pb-acid (all types) have levelled-off [15].

Sales of Ni-Cd and Ni-MH batteries are experiencing significant contractions, as will be detailed in the next section. Both are losing shares in favor of Li-ion.

In terms of applications, excluding the motive ones, sales of secondary batteries mainly concern: power tools, portable electronics, medical devices, communications, emergency power and the military/aerospace field. Primary batteries are especially requested in games and toys, lighting/home and communications.

Some of the big battery producers have transferred significant shares of their production to China, Korea and other Asian countries, where the cost of labor is obviously lower. This creates some problems when assigning the production on a geographic basis.

By the year 2006, the battery demand is expected to reach 60 billion dollars, this resulting in an increment of about 50% with respect to the 2003 values [174]. It is also forecast that the consumer battery demand will outperform other segments through 2006.

Typical portable devices are listed in Table 2.1. They can use primary and/or rechargeable batteries. Devices commonly encompassed in the definitions of consumer electronics, *e.g.* cell phones, notebooks, cameras, video

recorders, *etc.*, only use rechargeable batteries. Therefore, a closer look to the market related to these batteries is important.

## 10.2. The Market of Rechargeable Batteries for Portable Devices

A more complete list of high-end portable electronic devices include the following: PDAs, cellular and cordless phones, portable PCs, video cameras (movie), portable AV (audio-visual) equipment, digital still cameras (DSC). In addition, the important segment of power tools (*e.g.* drills, hammers, saws, screwdrivers, planers, *etc.*) has to be taken into account.

Ni-Cd or Ni-MH or Li-ion batteries power the above devices. The market trend of these batteries from 1985 to 2003 is shown in Figure 10.1 [175]\*. This figure needs some comments and explanations. From 1991 to 2000 the annual growth (AAGR) was 13%. The sales drop in 2001 was readily recovered: in 2002, there was an increment of 10% over 2001, and in 2003 an increment of 20% over 2002. Both Ni-Cd and Ni-MH are losing market shares in favor of

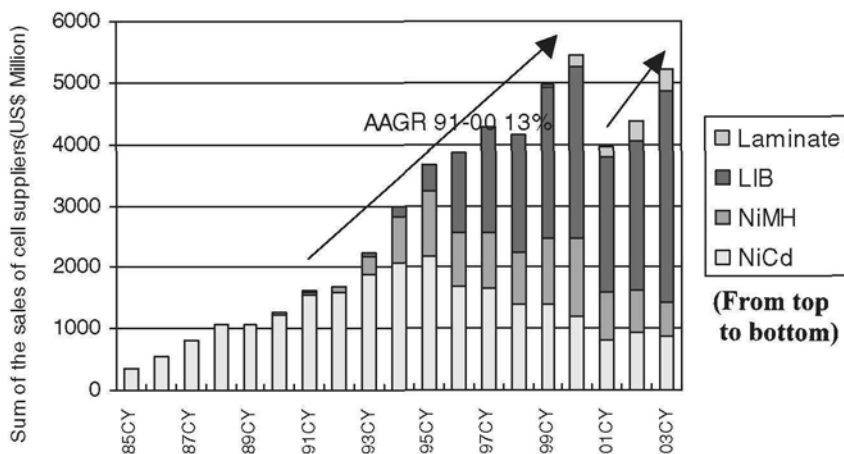


Figure 10.1. Worldwide sales of rechargeable batteries (in US dollars). CY = Calendar Year; LIB = Li-ion batteries; Laminate = thin LIB. (From Ref. 175)

\*As this figure and the following ones are derived from color figures, the grey bars may cause some misunderstandings. Therefore, the author will add indications to make reading easier.

Li-ion. The term *laminate* indicates thin (usually <3 mm) Li-ion batteries, mostly of the polymer type and with Al prismatic case. In 2003, the total market size was 5237 US million dollars (M\$), with Li-ion batteries (including the laminate ones) reaching 3821 M\$, *e.g.* 73%. The percentage of Li-ion in cellular phones, portable PC and video recorders was 90% at the end of 2003. These batteries are increasingly used also in digital cameras, games, AV equipment and power tools. Japanese companies shared 66% of the sales of Li-ion batteries in 2003. In Section 10.3, the major producers of these batteries will be mentioned.

The demand of Ni-MH batteries, as mentioned above, is decreasing. These batteries are losing shares in cellular phones and notebooks, and are not replacing Ni-Cd in power tools and cordless phones. The demand by application from 2000 to 2003 is reported in Figure 10.2 [176]. The data related to 2003 (680 million cells) was provisional, as it was obtained before the end of that year. The correct value calculated in 2004 is 630 M cells.

Ni-Cd batteries keep a satisfactory demand for power tools, cordless phones and portable AV equipment, as shown in Figure 10.3. Since 2002, these

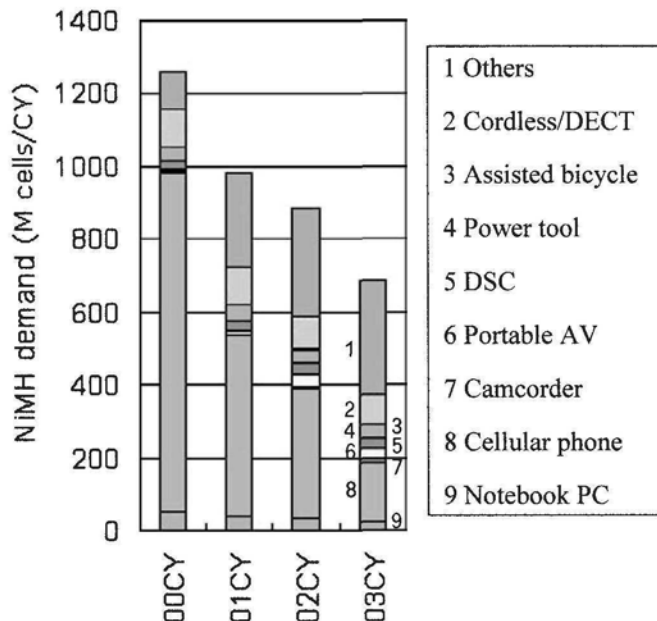


Figure 10.2. Trend of the sales of Ni-MH batteries from 2000 to 2003 by application. The numbers of the legend correspond to those of the bar. (From Ref. 176)

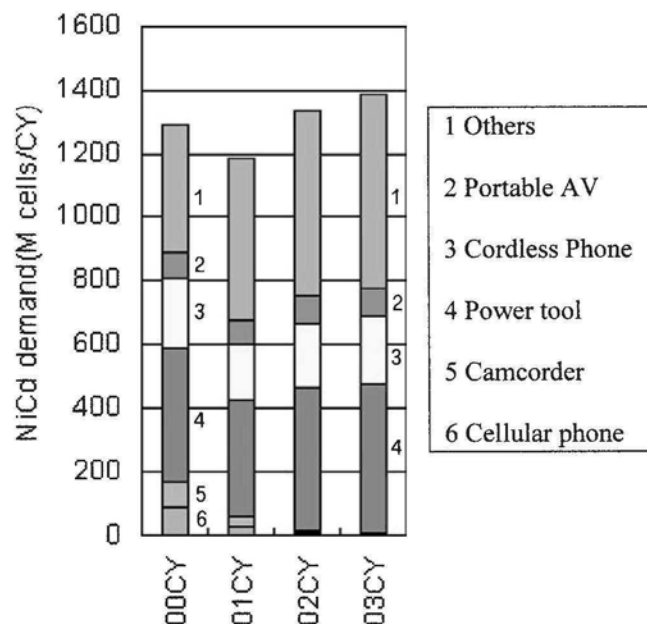


Figure 10.3. Trend of the sales of Ni-Cd batteries from 2000 to 2003 by application. The numbers of the legend correspond to those of the bars. (From Ref. 176)

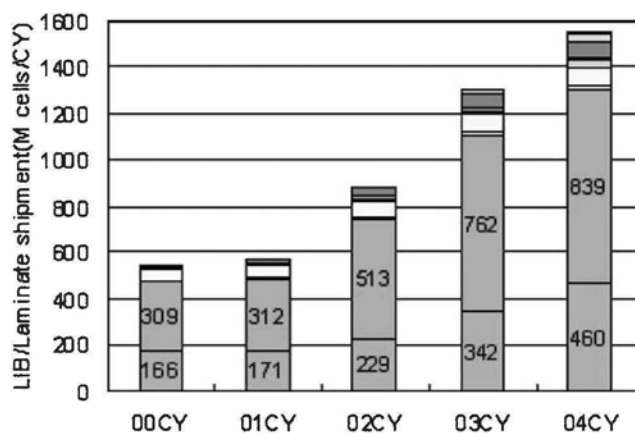


Figure 10.4. Trend of the sales of Li-ion batteries from 2000 to 2004 by application. Laminate cells are enclosed. Lowest segment of each bar: portable PCs, following segment: cell phones. Among the other applications, camcorders and cameras have the highest sales. (From Ref. 175)

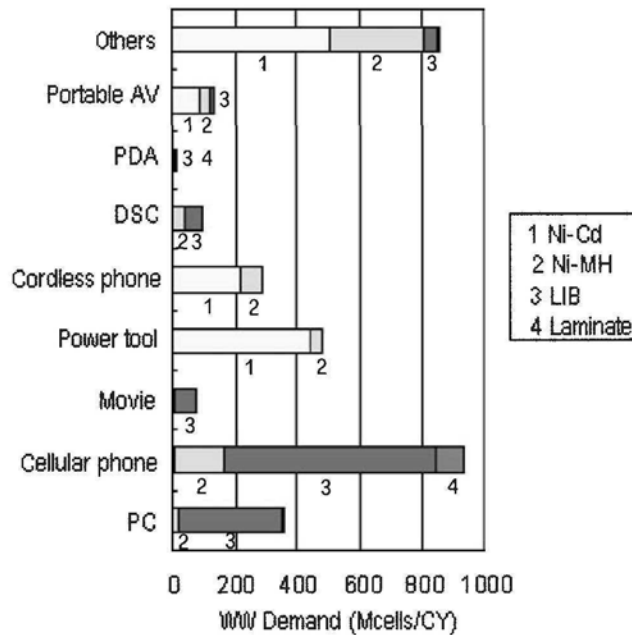


Figure 10.5. Demand of Ni-Cd, Ni-MH and Li-ion batteries in 2003 by application. The numbers of the legend correspond to those of the bars. (From Ref. 175)

batteries are no longer used in cellular phones and camcorders. In this case too, the provisional data for 2003 (1380 M cells) has to be corrected: 1270 M cells have been counted in 2004.

The trend for Li-ion batteries, including the laminate ones, is shown in Figure 10.4. The value for 2004 is provisional, as it was calculated in the same year. In the period 2001-2004, the annual growth rate was ~25%. No other primary or secondary battery can approach this rate.

A direct comparison of the demand by application for the three chemistries, in the year 2003, is shown in Figure 10.5. Laminate Li-ion are mainly used in cellular phones and PDAs (see also Figure 10.6). Portable computers, cellular phones and camcorders rely to a large extent on conventional Li-ion, as can be better appreciated in Figure 10.6. This figure also shows that, in power tools, some improved, high-power Li-ion can be used.

The tremendous growth of Li-ion batteries in the market is also based on the rapid fall of their price, especially on a Wh basis, as shown in Figure 10.7.

### 10.3. Lithium-Ion Batteries

Among the present batteries for portable electronic devices, the Li-ion one is certainly the winner of the market competition, as stressed by the data of the preceding section. Major companies are producing this kind of battery, with the Japanese ones leading the way, followed by Korean and Chinese companies. Sanyo is by far number one in terms of volume of batteries produced and sold, as shown in Figure 10.8. In 2003, Sanyo produced ~300 million cells. Two other Japanese companies, Sony and Matsushita, follow, while Korea occupies the 4<sup>th</sup> and 6<sup>th</sup> position with Samsung and LG Chemical. China is rapidly growing and BYD is in the 6<sup>th</sup> position together with LGC.

Anyway, the production is concentrated in Asia, as shown in Figure 10.9. China and Korea have gained significant market shares, while part of the Japanese production itself has been shifted to China.

Prismatic Li-ion cells are now widely used in small devices. Preferred sizes are 30x48 mm and 34x50 mm (WxL). 95% of these cells have thicknesses <8 mm, and the laminate ones (<3 mm) formed 15% of the total in 2004. Laminate cells are used, apart from phones and PDAs, in portable DVDs and in

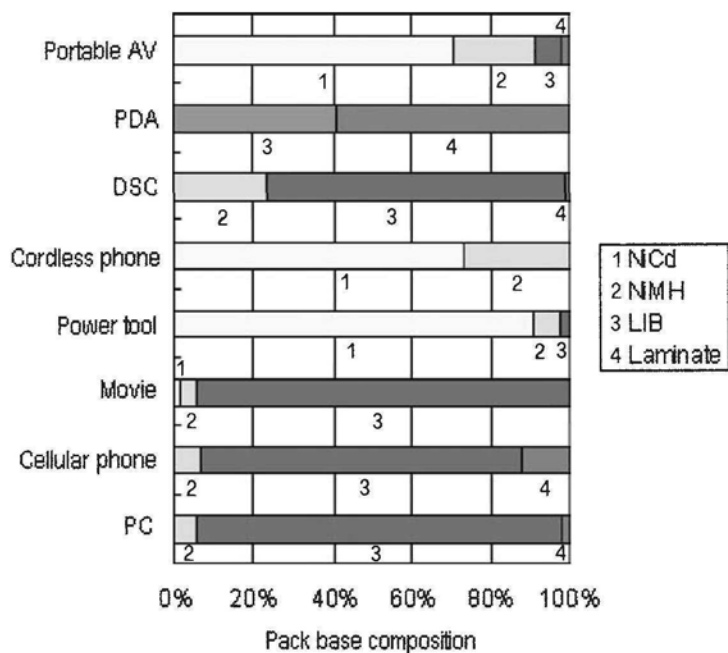


Figure 10.6. Percentage of a given battery chemistry in each application (2003). (From Ref. 175)

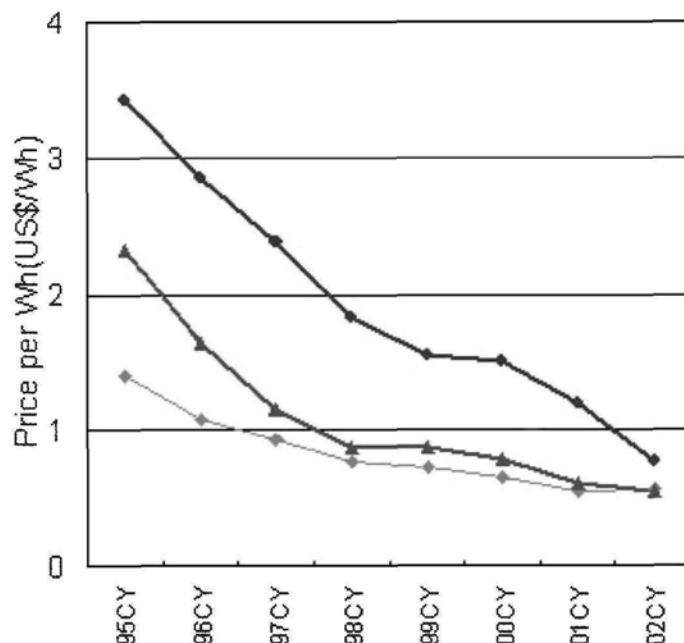


Figure 10.7. Trend of the average prices of Li-ion (including polymer types) (top), Ni-MH (middle) and Ni-Cd (bottom) in US \$ per Wh. (From Ref. 176)

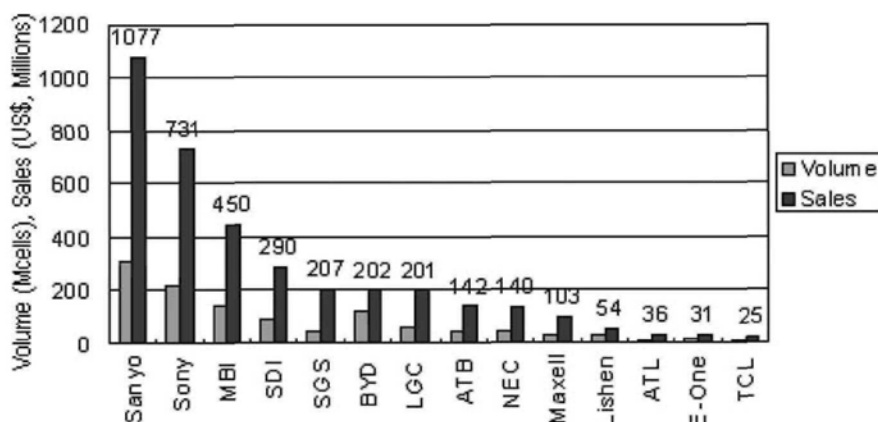


Figure 10.8. Volumes and sales of Li-ion cells in 2003. MBI: Matsushita (Panasonic), SDI: Samsung, SGS: Sanyo-GS, ATB: Asahi&Toshiba, ATL: Amperex Technology, TCL: TCL Hyperpower Batteries. See Appendix G for more information on these companies. (From Ref. 175)



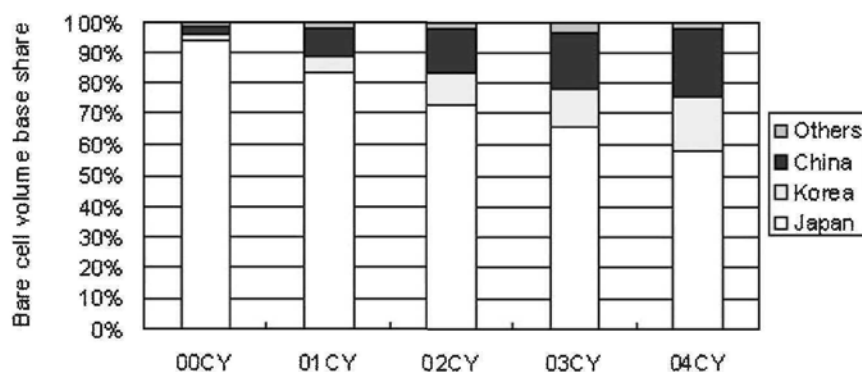


Figure 10.9. Subdivision of the Li-ion batteries production per nation (2000-2004). (From Ref. 175)

Bluetooth devices. Sony is the major producer of these cells, with a share of ~40% in 2004. Their price has been steadily decreasing and ranged between 1.3

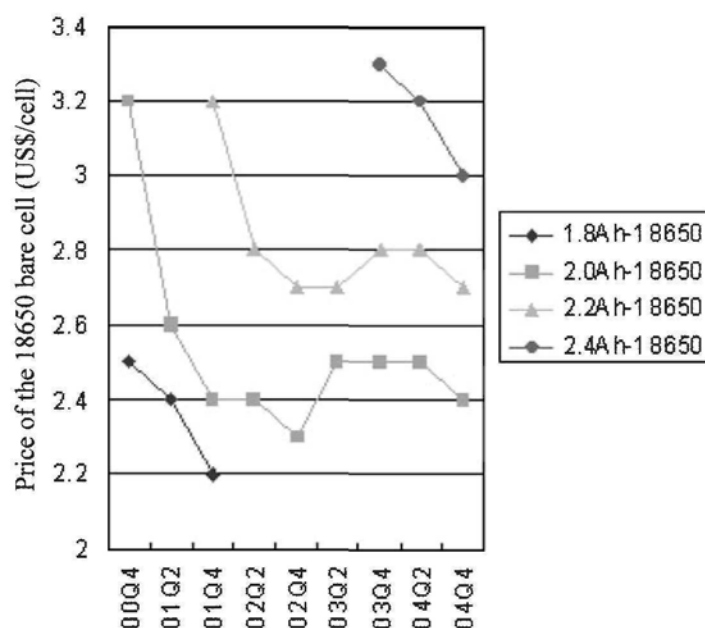


Figure 10.10. Price trend of 18650 Li-ion bare cells with different capacities. Q2=2<sup>nd</sup> quarter, Q4 = 4<sup>th</sup> quarter of the year. (From Ref. 175)

and 2.3 US\$/bare cell in the first quarter of 2004. Obviously, the price is higher in packs containing cells with control electronics, as mentioned in Chapter 7.

As far as laptop computers are concerned, Sanyo is the major producer with 1.2 million batteries per month produced by the end of 2003. Sony and Matsushita follow with 1.0 and 0.5 million batteries, respectively.

The demand for cylindrical Li-ion batteries is still very high, and the 18650 size is the preferred one. In the first quarter of 2004, 35 millions/month of 18650 cells were supplied. The majority of these, ~57%, had a capacity of 2.2 Ah, but cells with 2.4 Ah are gaining market shares. The trend of the price of 18650 cells with different capacities is shown in Figure 10.10. For all capacities, the initial price has always been decreasing. However, one can note for the two most popular capacities, 2.0 and 2.2 Ah, some price increments in 2003. The point is that the cost of the cathode,  $\text{LiCoO}_2$ , has increased from 23 to 40 US\$/kg. The last price is intended for the major manufacturers (e.g. Sanyo, Sony, etc.), while for other manufacturers the price may be higher than 50 \$/kg.

The higher cost of  $\text{LiCoO}_2$  is unlikely to result in the future in higher prices for Li-ion batteries with this cathode, as the OEMs will not accept this.

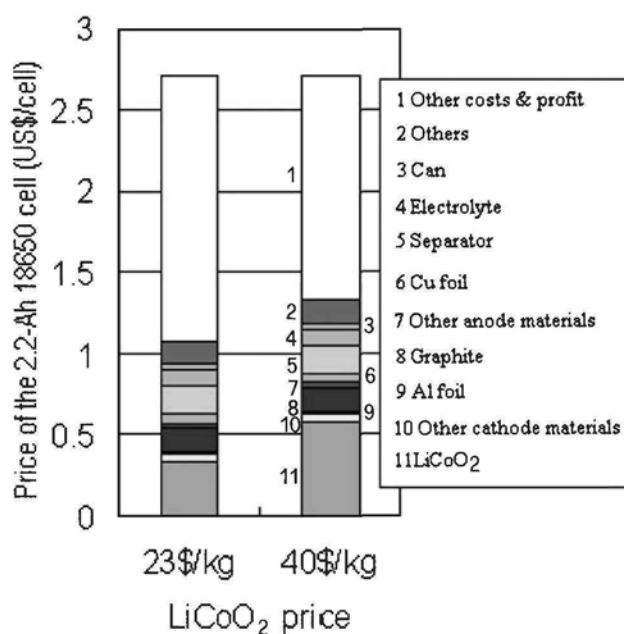


Figure 10.11. Items forming the price of the 2.2-Ah 18650 cell. The numbers of the legend correspond to those of the bar. (From Ref. 175)

It has been calculated that the price of a 2.2-Ah 18650 cell would increase by 0.25 US\$ with the above increase in the  $\text{LiCoO}_2$  cost. This is depicted in Figure 10.11. To keep the present price of 2.7 dollars, the profit of the manufacturers and dealers has to be reduced accordingly. In some Li-ion batteries, *e.g.* those with polymer electrolytes and Mn spinel cathodes, which are intrinsically safer, the absence of a sophisticated control/management circuit allows to cut the prices.

The provision is that in the near future the energy delivered by the 18650 cell will level off, both in terms of Wh/kg and Wh/L, while the cost per energy delivered (US\$/Wh) will decrease. This is shown in Figure 10.12, depicting the trends of energies and cost/energy from 1991 to 2005. In 2004, the specific energy of the 18650 cell has reached  $\sim 200$  Wh/kg, and the energy density  $\sim 520$  Wh/L. The same values are expected in 2005. When this cell was first marketed, in 1991, the cost/energy ratio was above 3 US\$/Wh. Since then, this ratio has constantly decreased and is forecast to go down to 0.28 \$/Wh by 2005. However, should the price of  $\text{LiCoO}_2$  continue to raise, the possibilities for alternative cathodes would obviously grow. In addition to  $\text{LiMn}_2\text{O}_4$ , such materials as, for example,  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  or  $\text{LiNi}_{1-x-y}\text{Co}_x\text{M}_y\text{O}_2$  ( $\text{M}=\text{Mg}$ ,  $\text{Mn}$  or  $\text{Al}$ ) could become more appealing by virtue of the lower cost of the elements substituting Co. The present cost of Ni-rich  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  and  $\text{LiMn}_2\text{O}_4$  is 10-12 US\$, well below the price of  $\text{LiCoO}_2$ .

The forecast for the long-term demand of Li-ion batteries is presented in Figure 10.13. By the year 2008, the demand will reach 2 billion cells per year. By the year 2013, the demand (2.5 Bcells/year) will be doubled with respect to that of 2003. The two dominating applications are and will be laptop computers (lowest segment of each bar in Figure 10.13) and cell phones (following segment). The present state-of-the-art of batteries for these two applications rules out the possibility that other batteries will be used.\*

## 10.4. Small Fuel Cells

By the second half of 2004, there was no real market for small fuel cells. Prototypes have been built and are under extensive tests, but probably the first ones will be on the market only in 2005. A German company, SFT, claims commercial production of low-watt fuel cells since September 2003 (see Chapter 8A). Their fuel cells are meant for recharging batteries, *e.g.* those

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\* Most of the content of Sections 10.2 and 10.3 has been derived from the reports of H. Takeshita (Japanese Institute of Information Technology [IIT]), at the 20<sup>th</sup> and 21<sup>st</sup> International Seminar&Exhibition on Primary&Secondary Batteries (Ft. Lauderdale, Florida, U.S.A.).

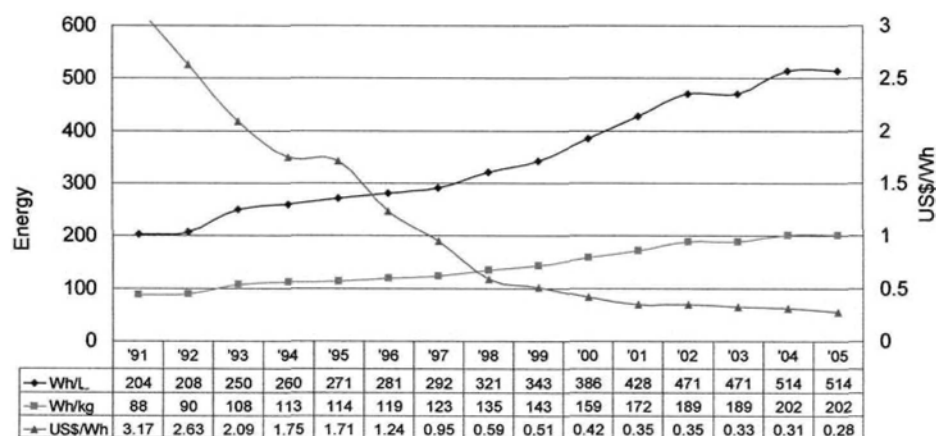


Figure 10.12. Energy density (Wh/L) (upper curve), specific energy (Wh/kg) (lower curve) and price/energy ratio (US \$/Wh) (decreasing curve) for the 18650 cell. (From Ref. 175)

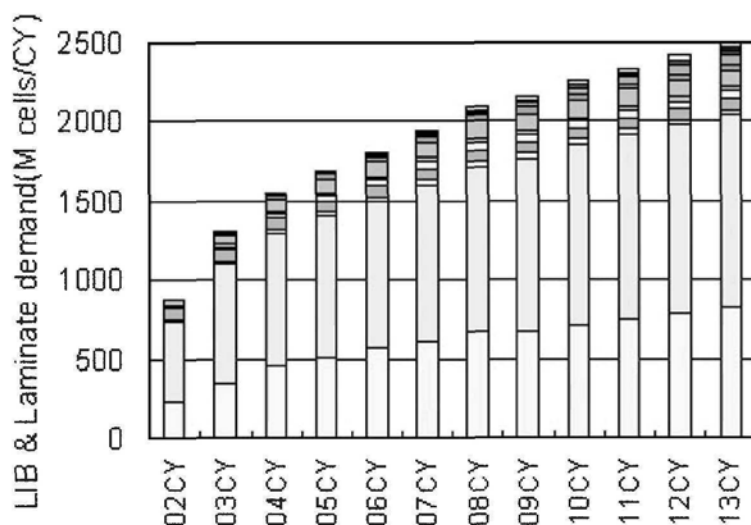


Figure 10.13. Long-term forecast for the demand of Li-ion batteries (including the laminate types). Lowest segment in each bar: laptop computers, following segment: cellular phones. (From Ref. 175)

powering portable computers, and their main product is a bulk cell weighing 9.7 kg.

As anticipated in Chapter 8A, considerations based on price, performance (energy and power), durability and weight/volume characteristics do not allow foreseeing for the near future a real competition between fuel cells and batteries.

## Appendix A

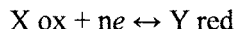
### Standard Electrode Potentials

In a battery, the chemical energy of the electrode materials is transformed into electrical energy. Therefore, at each electrode, a change in the energy content (or free energy) occurs during the oxidation or reduction process. This can be expressed by the relation:

$$-\Delta G = nEF \quad (1)$$

where:  $n$  = number of electrons involved in the oxidation (reduction) reaction,  $E$  = electrode potential, and  $F$  = Faraday's constant (96490 coulomb or 26.8 Ah).

Let us write a generic electrode reaction as:



where  $ox$  is the oxidized form of an active electrode material and  $red$  its reduced form (*e.g.* the couple  $Zn^{2+}/Zn$ ).

The free energy variation of this reversible process, characterized by an equilibrium constant  $K$ , can be expressed as:

$$\Delta G = \Delta G^\circ + RT \cdot \ln([red]^Y/[ox]^X) \quad (2)$$

where  $\Delta G^\circ (= -RT \cdot \ln K)$  is the free energy change in standard conditions, *i.e.* 25°C and 1 atm.

Combining eqs (1) and (2), one obtains:

$$E = -\Delta G^\circ/nF - (RT/nF) \cdot \ln([red]^Y/[ox]^X) \quad (3)$$

where  $\Delta G^\circ/nF$  is constant. At 25°C and 1 atm, this constant is set equal to  $E^\circ$ , the standard electrode potential, and eq (3) becomes:

$$E = E^\circ + (0.059/n) \cdot \log([ox]^X/[red]^Y)$$

(with  $R=8.31$  joules).

By using the activities instead of the concentrations ( $a = \gamma \cdot [c]$ , where  $\gamma$  is the activity coefficient and  $c$  the analytical concentration), eq (3) becomes:

$$E = E^{\circ} + (0.059/n) \cdot \log(a_{\text{ox}}^X/a_{\text{red}}^Y)$$

If the activities are equal to 1,  $E = E^{\circ}$ .

Each potential is measured vs. a reference electrode, e.g. the standard hydrogen electrode. This is ideally formed by a Pt-coated Pt plate, onto which  $\text{H}_2$  is bubbled, in a  $\text{H}^+$ -containing solution. For unit values of  $\text{H}_2$  pressure and  $\text{H}^+$  activity, at  $25^{\circ}\text{C}$ , the reference electrode is standard.

## APPENDIX B

### Frequently Used Symbols and Their Relations\*

- $I$  = Current expressed in amperes  
 $V$  = Electromotive force (emf) expressed in volts  
 $W$  = Power expressed in watts  
 $R$  = Resistance expressed in ohms  
 $Wh$  = Watt-hours  
 $T$  = Time expressed in hours

Formulas and Relationships	
Cell Capacity	$IT$
Cell Energy	$Wh = IVT$
Power	$W = IV = I^2R$
Resistance of a Conductor	$R = V/I$ (Ohm's Law)
Current (Cells in Parallel)	$I = I_1 + I_2 + \dots I_n$
Total Resistance (Cells in Parallel)	$1/R = 1/R_1 + 1/R_2 + \dots 1/R_n$
Voltage (Cells in Parallel)	$V = V_1 = V_2 = \dots V_n$
Current (Cells in Series)	$I = I_1 = I_2 = \dots I_n$
Total Resistance (Cells in Series)	$R = R_1 + R_2 + \dots R_n$
Voltage (Cells in Series)	$V = V_1 + V_2 + \dots V_n$

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\* From Ref. 31



## **APPENDIX C**

### **Acronyms Used in Electronics and Mentioned in This Book**

**CD** Compact Disk  
**CDA** Compact Digital Audio  
**CMOS** Complementary Metal Oxide Semiconductor  
**DSC** Digital Still Camera  
**DVC** Digital Video Camcorder  
**DVD** Digital Video Disc  
**FA** Frequency Analyzer  
**FET** Field Effect Transistor  
**GPS** Global Positioning System  
**GSM** Global Systems for Mobile Communications  
**HT** Handy Terminal  
**LCD** Liquid Crystal Display  
**LED** Light Emitting Diode  
**MD** Mini Disk  
**MOSFET** Metal Oxide Semiconductor FET  
**OA** Office Automation  
**PDA** Personal Digital Assistant  
**PHS** Portable Handy System  
**RTC** Real Time Clock

## APPENDIX D\*

### Glossary

<b>AB<sub>5</sub></b>	A metal alloy (e.g., LaNi <sub>5</sub> ) capable of undergoing a reversible hydrogen absorption/desorption reaction as the battery is charged and discharged, respectively.
<b>Absorption</b>	The taking up or retention of one material by another by chemical or molecular action.
<b>Active Material</b>	Specific chemically reactive material at the positive or negative electrode that takes part in the charge and discharge reactions.
<b>Air Cell</b>	Battery system which utilizes oxygen in combination with catalyzed carbon as the cathode and zinc as the anode.
<b>Alloy</b>	A mixture of several other metals or a metal and a non-metal.
<b>Ambient Humidity</b>	The average humidity of the surroundings.
<b>Ambient Temperature</b>	The average temperature of the surroundings.
<b>Ampere-Hour Capacity</b>	The quantity of electricity measured in ampere-hours (Ah) which may be delivered by a cell or battery under specified conditions.
<b>Anode</b>	The electrode in an electrochemical cell where oxidation takes place. During discharge, the negative electrode of the cell is the anode. During charge, the positive electrode is the anode.
<b>Battery or Pack</b>	Two or more electrochemical cells electrically interconnected in an appropriate series/parallel arrangement to provide the required operating voltage and current levels. Under common usage, the term "battery" is often also applied to a single cell.
<b>Bobbin</b>	A cylindrical cell design utilizing an internal cylindrical electrode, and an external electrode arranged as a sleeve inside the cell container.
<b>C-Rate (also see Hourly Rate)</b>	Discharge or charge current, in amperes, expressed in multiples of the rated capacity. For example, C/10 discharge current for a battery rated at 1.5 Ah is: 1.5 Ah/10 = 150 mA (A cell's capacity is not the same at all discharge rates and usually increases with decreasing rate).

<b>Capacity</b>	The total number of ampere-hours that can be withdrawn from a fully charged cell or battery under specified conditions of discharge.
<b>Capacity Density</b>	The ratio of the capacity of a battery to its volume (Ah/L).
<b>Capacity Retention (or Charge Retention)</b>	The fraction of the full capacity available from a battery under specified conditions of discharge after it has been stored for a period of time.
<b>Carbon Zinc</b>	A generic term for primary dry batteries of the Leclanché or zinc chloride systems.
<b>Cathode</b>	The electrode in an electrochemical cell where reduction takes place. During discharge, the positive electrode of the cell is the cathode. During charge, the negative electrode is the cathode.
<b>Cell</b>	The basic electrochemical unit used to generate or store electrical energy.
<b>Cell Reversal</b>	Reversing polarity of terminals of a cell or battery due to overdischarge
<b>Charge</b>	The conversion of electrical energy, provided in the form of electrical current from an external source, to restore the chemical energy in a cell or battery.
<b>Charge Control</b>	Technique for effectively terminating the charging of a rechargeable battery.
<b>Closed-Circuit Voltage (CCV)</b>	The potential or voltage of a battery when it is discharging or charging.
<b>Constant Current Discharge</b>	A battery discharge regime whereby the current drawn during the discharge remains constant.
<b>Constant Power Discharge</b>	A battery discharge regime whereby the current during the discharge increases as the battery voltage decreases.
<b>Constant Resistance Discharge</b>	A battery discharge regime whereby the resistance of the equipment load remains constant throughout discharge.
<b>Continuous Test</b>	A test in which a battery is discharged to a prescribed end-point voltage without interruption.
<b>Coulomb</b>	The amount of electricity transported by a current of one ampere flowing for one second.
<b>Current Collector</b>	An inert structure of high electrical conductivity used to conduct current from or to an electrode during discharge or charge.

<b>Current Density</b>	The current per unit active area of the surface of an electrode.
<b>Current Drain</b>	The current withdrawn from a battery during discharge.
<b>Cut-off Voltage</b> (also see End Voltage)	The battery voltage at which the discharge is terminated. The cut-off voltage is specified by the battery manufacturer and is generally a function of discharge rate.
<b>Cycle</b>	A charge/discharge sequence.
<b>Cycle Life</b>	The number of cycles under specified conditions which are available from a secondary battery before it fails to meet specified criteria as to performance.
<b>Depth of Discharge (DOD)</b>	The ratio of the quantity of electricity (usually in ampere-hours) removed from a battery to its rated capacity.
<b>Desorption</b>	The opposite of absorption, whereby the material retained by a medium or another material is released.
<b>Discharge</b>	The conversion of the chemical energy of a battery into electrical energy, and the withdrawal of the electrical energy into a load.
<b>Discharge Rate</b>	The rate, usually expressed in amperes, at which electrical current is taken from the battery.
<b>Drain</b>	The current withdrawn from a battery during discharge.
<b>Dry Cell</b>	A cell with immobilized electrolyte. The term "dry cell" is often used to describe the Leclanché cell.
<b>Duty Cycle</b>	The operating regime of a battery including factors such as charge and discharge rates, depth of discharge, cycle duration, and length of time in the standby mode.
<b>E-Rate</b>	Discharge or charge power, in watts, expressed as a multiple of the rated energy of a cell or battery, which is expressed in watt-hours. For example, the E/10 rate for a cell or battery rated at 17.3 watt-hours is 1.73 watts. (This is similar to the method for calculating C-Rate.)
<b>Electrochemical Equivalent</b>	Weight of a substance that is deposited at an electrode when the quantity of electricity which is passed is one faraday (96490 coulombs).
<b>Electrode</b>	The site, area or location at which electrochemical processes take place.
<b>Electrolyte</b>	The medium which provides the ion transport mechanism between the positive and negative electrodes of a cell.

<b>End Voltage (also see Cut-off Voltage)</b>	The prescribed voltage at which the discharge (or charge, if end-of-charge voltage) of a battery may be considered complete.
<b>Energy</b>	The output capability of a cell or battery, usually expressed in watt-hours.
<b>Energy Density</b>	The ratio of the energy available from a battery to its volume (Wh/L).
<b>Forced Discharge</b>	Discharging a cell in a battery, by the other cells or an external power source, below zero volts into voltage reversal.
<b>Fuse</b>	Device used for cutting off an electrical current in the event of an abusive condition.
<b>Gassing</b>	The evolution of gas from one or more of the electrodes in a cell. Gassing commonly results from local action (self-discharge) or from the electrolysis of water in the electrolyte during charging.
<b>Gravimetric Energy Density</b>	The ratio of the energy output of a cell or battery to its weight (Wh/kg). This term is used interchangeably with specific energy.
<b>Hazardous Waste</b>	Waste which is classified as "hazardous" ( <i>i.e.</i> , potentially harmful to the environment and human health) by the government.
<b>Hertz</b>	The standard unit of frequency. A frequency of one complete cycle per second is a frequency of one hertz.
<b>Hourly Rate (also see C-Rate)</b>	A discharge rate, in amperes, of a battery which will deliver the specified hours of service to a given cut-off voltage.
<b>Intermittent Test</b>	A test during which a battery is subjected to alternate periods of discharge and rest according to a specified discharge regime.
<b>Internal Impedance</b>	The opposition exhibited by a circuit element (cell or battery) to the flow of an alternating current (AC) of a particular frequency as a result of resistance, inductance and capacitance.
<b>Internal Resistance (IR)</b>	The opposition exhibited by a circuit element to the flow of direct current (DC). In a cell, the internal resistance is the sum of the ionic and electronic resistances of the cell components.
<b>IR Drop</b>	A voltage drop associated with the electrical resistance (R) of a battery or current flow (I). The voltage drop is the product of the current (in amperes) and the resistance (in ohms).
<b>Leclanché</b>	A carbon zinc cell with slightly acidic electrolyte consisting of $\text{NH}_4\text{Cl}$ and $\text{ZnCl}_2$ in water
<b>Limiting Current</b>	The maximum current drain under which the particular battery will perform adequately under a continuous drain.

<b>Memory Effect</b>	A phenomenon in which a cell or battery operated in successive cycles to the same, but less than full, depth of discharge temporarily loses the rest of its capacity at normal voltage levels.
<b>Metal Hydride</b>	An intermetallic compound or alloy in which hydrogen has been absorbed; also, the negative electrode in a nickel-metal hydride battery.
<b>Midpoint Voltage</b>	The voltage of a battery midway in the discharge between the start of the discharge and the end voltage.
<b>Miniature Cell</b>	A button or coin shaped cell. Its diameter is greater than its height
<b>Nominal Voltage</b>	The characteristic operating voltage or rated voltage of a battery.
<b>Open-Circuit Voltage (OCV)</b>	The difference in potential between the terminals of a cell when the circuit is open (no-load condition).
<b>Overcharge</b>	The forcing of current through a cell after all the active material has been converted to the charged state, that is, continued charging after reaching 100 percent state-of-charge.
<b>Overdischarge</b>	The process of discharging a cell or battery beyond its cut-off voltage and possibly into voltage reversal.
<b>Parallel</b>	Term used to describe the interconnection of cells or batteries in which all the like terminals are connected together. This results in increased capacity.
<b>Passivation</b>	The phenomenon by which a metal, although in conditions of thermodynamic instability, remains indefinitely unattacked because of modified or altered surface conditions.
<b>Polarity</b>	In electricity, the condition of being positive or negative.
<b>Polarization</b>	The lowering of the potential of a cell or electrode from its equilibrium value caused by the passage of an electric current.
<b>Positive Temperature Coefficient (PTC)</b>	A thermally reactive device which becomes highly resistive at a specific temperature or current.
<b>Primary Battery</b>	A battery which is not intended to be recharged and is discarded when the battery has delivered all of its electrical energy.
<b>Pulse Current</b>	A periodic current drain of higher than normal drain rates.
<b>Rated Capacity</b>	The number of ampere-hours a battery can deliver under specific conditions ( <i>e.g.</i> , rate of discharge, end voltage, temperature); usually specified by the battery manufacturer.

<b>Rechargeable (or "Secondary") Battery</b>	A galvanic battery which, after discharge, may be restored to the fully charged state by the passage of an electrical current through the cell in the opposite direction to that of discharge.
<b>Reversal</b>	The changing of the normal polarity of a battery due to overdischarge.
<b>Safety Vent</b>	A venting mechanism designed into a cell which activates under specific conditions of abuse to relieve internal pressure.
<b>Secondary Battery</b>	A battery designed to be recharged
<b>Secure Waste Landfill</b>	A landfill designed for disposal of normal household trash but which meets government standards designed to protect the environment.
<b>Self-Discharge</b>	The loss of useful capacity of a battery on storage due to internal chemical action (local action).
<b>Separator</b>	An ionic permeable and electronically nonconductive spacer or material which prevents electronic contact between electrodes of opposite polarity in the same cell.
<b>Series</b>	The interconnection of cells in such a manner that the positive terminal of the first is connected to the negative terminal of the second, and so on, resulting in increased voltage.
<b>Service Life</b>	The period of useful life of a battery before a predetermined end-point voltage is reached.
<b>Shelf-Life</b>	The duration of storage under specified conditions at the end of which the battery still retains the ability to give a specified performance.
<b>Short-Circuit Current (SCC)</b>	The initial value of the current obtained from a battery in a circuit of negligible resistance.
<b>Specific Energy</b>	The ratio of the energy output of a cell or battery to its weight (Wh/kg). This term is used interchangeably with gravimetric energy density.
<b>Spiral Wound</b>	An electrode structure of high surface area created by winding the electrodes and separator into a spiral-wound, jelly-roll configuration.
<b>State of Charge (SOC)</b>	Conditions in terms of the rated capacity remaining at a given point in time.
<b>State of Health (SOH)</b>	Percentage of the rated capacity actually delivered by a cell

<b>Temperature Cut-off (TCO)</b>	A protective or safety device ( <i>e.g.</i> , thermostat, PTC, <i>etc.</i> ) which senses temperature ( <i>e.g.</i> , in a battery) and opens or cuts off the electrical circuit if the specified temperature is exceeded, thus preventing a further rise in temperature due to the charge or discharge of a battery.
<b>Thermistor</b>	A temperature sensitive resistor, usually made from specially processed oxides.
<b>Thermostat</b>	A temperature sensitive switch.
<b>Top-Up Charge</b>	A low rate charge following the main charge, designed to ensure maximum capacity.
<b>Trickle Charge</b>	A charge at a low rate, balancing losses through local action and/or periodic discharge, to maintain a cell or battery in a fully charged condition.
<b>Voltage Depression</b>	An abnormal drop in voltage below expected values during the discharge of a battery.
<b>Voltage Delay</b>	Time delay for a battery to deliver the required operating voltage after it is placed under load.
<b>Voltage-Keyed</b>	A system which incorporates a mechanical identifier on batteries and devices to ensure only batteries of the correct voltage are connected to the device.
<b>Voltage Reversal</b>	The changing of the normal polarity of a battery due to overdischarge.
<b>Volumetric Energy Density</b>	The ratio of the energy output of a cell or battery to its volume (Wh/L).
<b>Working Voltage</b>	The typical voltage or range of voltage of a battery during discharge (also called operating voltage or running voltage).

\* From Ref. 177



## Appendix E

### Safety Considerations

#### 1. Some General Safety Considerations\*

- Locate batteries as far away as possible from any heat source to prevent service degradation.
- Mind the battery connection. If a battery is inserted backwards in parallel or series/parallel wiring or in some series connections, leakage and/or battery rupture may occur.
- If metal-jacketed batteries are used, isolate the metal jacket from any material that can conduct electricity and prevent any potential short circuit.
- Only use recommended batteries and carefully follow all instructions and warnings on the battery label and package.
- Replace all batteries at one time. The replacement of a partial set or mixing batteries from different chemical systems exposes the device to the possibility of electrolyte leakage and damage through over-discharge of the lower capacity batteries.
- Batteries that are not specifically designed to be recharged can leak and, in some cases, rupture if recharged.
- Do not heat or open batteries. This will expose the user to chemical burns or, in rare cases, battery ruptures.
- Check the batteries' effectiveness frequently, particularly in devices that are depended upon for personal safety. Batteries should be replaced as soon as their performance becomes unsatisfactory.
- Make sure that the contact surfaces are visually clean and bright when installing new batteries.
- Remove the batteries if the device will not be used for several months.

#### 2. Zinc-Carbon and Alkaline Batteries\*

##### *Storage Conditions*

Batteries should be stored at temperatures between 10°C and 25°C, with relative humidity not exceeding 65%. Refrigeration of these batteries is not necessary because of their very good capacity retention. Excessive temperature cycling and storage at temperatures greater than 25°C should be avoided to maximize shelf-life.

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\* Courtesy of Energizer/Eveready

***Proper Usage and Handling***

- Discharged batteries should be removed from equipment to prevent possible damage.
- Batteries should be removed from a device when it is not expected to be in use for several months.
- Batteries should also be removed from equipment while it is being powered by household (AC) current.
- Always replace all batteries at the same time since batteries in series, in different states of discharge, may eventually drive the weakest battery into voltage reversal with progressive risk of leakage or rupture.
- Mixing battery systems, such as alkaline with zinc-carbon, may result in voltage reversal and should be avoided.
- Always replace the battery or batteries in your equipment with the size and type of battery specified by the equipment manufacturer.
- Keep batteries away from small children. If swallowed, consult a physician at once.

***Charging***

Zn-Carbon and alkaline Zn/MnO<sub>2</sub> are of the primary type and are not designed to be recharged. Attempts to recharge a battery may cause an imbalance within the cell, leading to gassing and possibly explosion on either charge or discharge cycles.

### **3. VRLA Batteries\***

***VRLA Battery Safety Concerns***

Maintenance and servicing of a VRLA battery should only be performed and supervised by personnel knowledgeable of lead-acid batteries. Personnel should also be knowledgeable of personal and equipment safety precautions. Keep unauthorized personnel away from the batteries during maintenance activities.

***VRLA Battery Electrical Hazards***

Battery systems present a risk of electrical shock and high current short circuits. The following precautions should be observed when maintaining VRLA batteries:

1. Remove all personal metal objects (watches, rings, *etc.*)
2. Use insulated tools.
3. Wear full eye protection and rubber gloves.
4. Observe circuit polarities.
5. Do not make or break live circuits.
6. Prior to handling batteries on a metal rack, assure the battery is not inadvertently grounded by observing the ground fault detector indicator. In its absence, measure the voltage between the battery and the rack. It should be zero. If not, determine the cause

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\* Courtesy of ESB Batteries

and correct prior to proceeding.

6. Do not lay metal tools and hardware on top of the batteries.

7. As appropriate, use an insulating blanket to cover exposed portions of the battery system when performing extended maintenance that could result in personal or equipment contact with the energized conductors.

Certain types of rectifier circuits used in charging the VRLA battery may not include a line isolating transformer. In these cases, extreme caution should be exercised when maintaining and collecting data on the battery system.

VRLA batteries are sometimes enclosed in cabinets with very limited access. Again, extreme caution must be exercised when maintaining and collecting measurements on the battery system.

### ***VRLA Battery Recycling & Disposal***

Lead acid batteries are to be recycled. Batteries contain lead and dilute sulfuric acid. Dispose of the battery in accordance with local regulations. Do not dispose of the battery in a landfill, lake or other unauthorized location.

### ***VRLA Battery Chemical Hazards***

Any gelled or liquid emissions from a VRLA battery is electrolyte which contains dilute sulfuric acid that is harmful to the skin and eyes. The electrolyte is also electrically conductive and corrosive.

If the electrolyte contacts the skin, wash the area immediately and thoroughly with water. If the electrolyte enters the eyes, wash your eyes thoroughly for a 10-minute period with clear water or a special neutralizing eye wash solution and seek immediate medical attention.

Neutralize any spilled electrolyte with the special solution contained in a "spill kit" or with a solution of 1 pound of sodium bicarbonate in 1 gallon of water.

### ***Fire, Explosion and Heat Hazards***

Lead acid batteries can contain an explosive mixture of hydrogen gas which can vent under overcharging conditions.

Do not smoke or introduce sparks in the vicinity of the battery.

Prior to handling the battery, touch a grounded metal object, such as the rack, to dissipate any static charge that may have developed on your body.

Do not charge batteries in a sealed container. The individual batteries should have 5 to 10 millimeters of space between them to allow for proper cooling. If contained, assure the container, cabinet or room has adequate ventilation to prevent an accumulation of potentially vented gas.

### ***VRLA Battery Warnings***

Do not attempt to remove the vents (valves) from a VRLA battery or add water. This procedure presents a safety hazard and voids the warranty.

#### 4. Cylindrical-type Primary Lithium Batteries\*

1. Do not use batteries for unspecified purposes.

Differences in voltage or terminal configuration may cause an imperfect connection, fire, heat generation, leakage or bursting.

2. Do not charge.

When this battery is charged, gas is generated inside and raises internal pressure, resulting in fire, heat generation, leakage or bursting.

3. Do not heat, disassemble nor dispose of in fire.

Doing so damages the insulation materials or the safety vent, resulting in...(see point 2).

4. Do not insert batteries with the (+) and (-) polarities reversed.

Make sure the polarities are in the right position when inserting the batteries into equipment. When using 3 or more batteries, the equipment may operate even though one of the batteries is improperly inserted. But this may cause leakage or bursting.

5. Do not short-circuit.

If the (+) and (-) come into contact with metal objects, short circuiting occurs resulting in heat generation or bursting. When carrying or storing batteries, avoid direct contact with metal objects such as bracelets or key chains by putting them in a separate bag.

6. Keep batteries out of children's reach.

If leaked liquid is ingested or a battery is swallowed, consult a physician immediately.

7. In case of leakage or a strange smell, keep away from fire to prevent ignition of any leaked electrolyte.

8. Do not use new and used batteries together. Do not use different types of batteries together.

Doing so may cause...(see point 2).

9. Do not solder directly.

Doing so may cause damage to insulation materials. It may also cause...(see point 2).

10. Do not apply strong pressure nor handle roughly.

Doing so may cause...(see point 2).

11. To prevent damage to the safety vent inside the battery, do not deform in any way.

12. Do not force-discharge.

When a battery is force-discharged by an external power source, the voltage drops to 0 or less (reversal voltage) and gas is generated inside the battery. This may cause...(see point 2).

13. Do not damage nor peel off the resin film on the surface of the battery.

The battery surface is covered with thin vinyl film to prevent short circuiting. Cutting with a knife or peeling off this film causes short circuiting, resulting in heat generation or bursting.

14. Keep batteries away from direct sunlight, high temperature and humidity.

Leaving batteries in such places may cause heat generation.

15. Be sure to wrap each battery when disposing or storing to avoid short circuit. Putting batteries together or in contact with metal objects causes short circuiting, resulting in fire, heat generation or bursting.

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\* Courtesy of Sanyo

16. Avoid contact with water.

This can cause heat generation.

17. Read the equipment instruction manual and precautions carefully before use. Some usages or types of equipment do not suit the specifications or performance of these batteries.

18. If leaked liquid gets in your eyes, wash them with clean water and consult a physician immediately.

## 5. Lithium-Ion Batteries\*

### *Danger*

1. Do not disassemble or modify the battery pack. The battery pack is equipped with built-in safety/protection features. Should these features be disabled, the battery pack can leak acid, overheat, emit smoke, burst and/or ignite.

2. Do not connect the positive (+) and negative (-) terminals with a metal object such as wire. Do not transport or store the battery pack together with metal objects such as necklaces, hair pins, *etc.* Otherwise, shortcircuiting will occur, overcurrent will flow, causing the battery pack to leak acid, overheat, emit smoke, burst and/or ignite, or the metal object such as wire, necklace or hair pin can generate heat.

3. Do not discard the battery pack into fire or heat it. Otherwise, its insulation can melt down, its gas release vent or safety features will be damaged and/or its electrolyte can ignite, possibly leading to acid leakage, overheating, smoke emission, bursting and/or ignition on it.

4. Do not use or leave the battery pack near a heat source such as a fire or a heater (80°C or higher). If the resin separator should be damaged owing to overheating, internal short-circuiting may occur to the battery pack, possibly leading to acid leakage, overheating, smoke emission, bursting and/or ignition of the battery pack.

5. Do not immerse the battery pack in water or seawater, and do not allow it to get wet. Otherwise, the protective features in it can be damaged, it can be charged with extremely high current and voltage, abnormal chemical reactions may occur in it, possibly leading to... (see point 4).

6. Do not recharge the battery pack near fire or in extremely hot weather. Otherwise, hot temperatures can trigger its built-in protective features, inhibiting recharging, or can damage the built-in protective features, causing it to be charged with an extremely high current and voltage, and, as a result, abnormal chemical reactions can occur in it, possibly leading to...(see point 4).

7. To recharge the battery pack, use the battery charger specifically designed for the purpose and observe the recharging conditions specified by the manufacturer. A recharging operation under non-conforming recharging conditions (higher temperature and larger voltage/current than specified, modified battery charger, *etc.*) can cause the battery pack to be overcharged, or charged with extremely high current, abnormal chemical reaction can occur in it, possibly leading to...(see point 4).

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\*Courtesy of Sanyo

8. Do not pierce the battery pack with a nail or other sharp objects, strike it with a hammer, or step on it. Otherwise, the battery pack will become damaged and deformed, internal short-circuiting can occur, possibly leading to...(see point 4).
9. Do not strike or throw the battery pack. The impact might cause leakage, overheating, smoke emission, bursting and/or ignition. Also, if the protective feature in it becomes damaged, it could become charged with an extremely high current and voltage, abnormal chemical reactions can occur, which can lead to...(see point 4).
10. Do not use an apparently damaged or deformed battery pack. Otherwise, acid leakage, overheating, smoke emission, bursting and/or ignition of the battery pack may occur.
11. Do not directly solder the battery pack. Otherwise, heat can melt down its insulation, damage its gas release vent or safety features possibly leading to...(see point 4).
12. Do not reverse the positive (+) and negative (-) terminals. Otherwise, during recharging, the battery pack will be reverse-charged, abnormal chemical reactions then may occur, or excessively high current can flow during discharging possibly leading to...(see point 4).
13. The positive (+) and negative (-) terminals are arranged in a particular orientation. Do not force the connection if you cannot easily connect the battery pack terminals to the battery pack charger or other equipment. Confirm that the terminals are correctly oriented. Reversing the terminals will result in reverse-charging, possibly leading to...(see point 4).
14. Do not connect the battery pack to an electrical outlet, vehicle cigarette lighter, *etc.* When subjected to large voltage, overcurrent can flow on the battery pack, possibly leading to...(see point 4).
15. Do not use the battery pack for a purpose other than those specified. Otherwise, its guaranteed performance will be lost and/or its service life will be shortened. Depending on the equipment in which the battery pack is used, excessively high current can flow through battery pack, possibly damaging it and leading to...(see point 4).
16. If the battery pack leaks and the electrolyte gets into the eyes, do not rub them. Instead, rinse the eyes with clean running water and immediately seek medical attention. Otherwise, eye injury may result.

### ***Warning***

1. Do not use the battery pack in combination with primary battery packs (such as dry-cell battery packs) or battery packs of different capacities or brands. Otherwise, the battery pack can be overdischarged during use or overcharged during recharging, abnormal chemical reactions may occur, possibly leading to acid leakage, overheating, smoke emission, bursting and/or ignition.
2. If recharging operation fails to complete even when a specified recharging time has elapsed, immediately stop further recharging. Otherwise, acid leakage, overheating, smoke emission, bursting and/or ignition can occur.
3. Do not put the battery pack into a microwave oven or pressurized container. Rapid heating or disrupted sealing can lead to...(see point 1).
4. If the battery pack leaks or gives off a bad odor, remove it from any exposed flame. Otherwise, the leaking electrolyte may catch fire, and the battery pack may emit smoke, burst or ignite.

5. If the battery pack gives off an odor, generates heat, becomes discolored or deformed, or in any way appears abnormal during use, recharging or storage, immediately remove it from the equipment or battery pack charger and stop using it. Otherwise, the problematic battery pack can develop...(see point 1).

### **Caution**

1. Do not use or subject the battery pack to intense sunlight or hot temperatures such as in a car in hot weather. Otherwise, acid leakage, overheating and/or smoke emission can occur. Also, its guaranteed performance will be lost and/or its service life will be shortened.
2. The battery pack incorporates built-in safety devices. Do not use it in a location where static electricity (greater than the manufacturer's guarantee) may be present. Otherwise, the safety devices can be damaged, possibly leading to acid leakage, overheating, smoke emission, bursting and/or ignition.
3. The guaranteed recharging temperature range is 0 to 40°C. A recharging operation outside this temperature range can lead to acid leakage and/or overheating of the battery pack, and may cause damage to it.
4. If acid leaking from the battery pack contacts your skin or clothing, immediately wash it away with running water. Otherwise, skin inflammation can occur.
5. Store the battery pack in a location where children cannot reach it. Also, make sure that a child does not take out the battery pack from the battery pack charger or equipment.
6. Before use, try to obtain and study the Operation Manual and Precautions.
7. For recharging procedures, refer to the Operation Manual of your battery pack charger.
8. If you find rust, a bad odor, overheating and/or other irregularities when using the battery pack for the first time, return it to your supplier or vendor.

(Note of the Author: As also stressed in Section 7.6, some accidents have been reported with Li-ion batteries, *e.g.* in cellular phones or portable computers. In most cases, these were low-cost, replacement batteries having not enough safety devices, or, anyway, not constructed in such a way to ensure maximum safety. The author does not recommend purchasing of such batteries: the user should always rely on the products of well known manufacturers).

## **6. Nickel-Cadmium and Nickel-Metal Hydride Batteries\***

### **Danger**

Failure to carefully observe the following procedures and precautions can result in battery leakage, heat generation, bursting and serious personal injury!

1. Never dispose of batteries in a fire or expose to high temperatures.

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\*Courtesy of Sanyo

2. Do not connect the positive (+) and negative (-) terminals of batteries together with electrically conductive material, including lead wires. Do not transport or store batteries with their uncovered terminals or connected with a metal necklace or other conductive material.
3. Only charge batteries using those special chargers that satisfy the manufacturer's specifications. Only charge batteries under the conditions specified by the manufacturer. Failure to follow proper charging procedures can result in damage to the batteries.
4. Never disassemble, modify or reconstruct batteries. Never solder lead wires directly on to batteries. Special order batteries, manufactured in accordance with the customer's equipment specifications, are packed by selected type and the number of assortments. Only use special order batteries in equipment for which they were specified.
5. The positive (+) and negative (-) polarities of batteries are predetermined. Do not force the terminal connection to a charger or equipment. If the terminals cannot be easily connected to the charger or equipment check if the (+) and (-) terminals are correctly positioned.
6. Do not directly connect batteries to a direct power source or the cigarette lighter outlet in a car.
7. The gas release vent is located at the positive (+) section of batteries. Never deform this section or cover or obstruct the gas release vent.
8. Batteries contain a strong colorless alkali liquid. The alkali is extremely corrosive and will cause skin damage. If any liquid from a battery comes in contact with the users' eyes, they should immediately flush their eyes with clean water and consult a doctor. The strong alkali can damage eyes and lead to permanent loss of eyesight.
9. When batteries are to be incorporated in equipment or housed within a case, avoid sealed structures, as this may lead to the equipment or case being damaged or may be harmful to users.

### ***Warning***

1. Do not apply water, seawater or other oxidizing agents to batteries, as this can cause rust and heat generation. If a battery becomes rusted, the gas release vent may no longer operate, and can result in bursting.
2. Never use batteries if they are leaking, deformed, discolored, damaged or otherwise differ from their normal condition. External damage to the batteries can be a sign of a malfunction.
3. Do not damage or remove the external tube of batteries, as this may cause leakage, heat generation or bursting.
4. Do not overcharge batteries by exceeding the predetermined charging period specified by the battery's charger's instructions or indicator. If batteries are not fully charged after the battery charger's predetermined charging period has elapsed, stop the charging process. Prolonged charging may cause leakage and heat generation and bursting. Be sure to handle recharged batteries carefully as they may be hot.
5. Strong alkali in the electrolyte may cause burns and be harmful if it comes to contact with skin. If so, wash the affected area with clean water immediately.
6. Do not connect more than 20 batteries in series, as this may cause electric shock, leakage or heat generation. Consult the manufacturer if designing a battery pack containing more than 20 cells.



7. When the usage time for a battery becomes extremely short after charging, its operating life has ended and it should be replaced.
8. Keep the equipment or batteries out of the reach of small children, in order to avoid them to swallow batteries. In the event the batteries are swallowed, consult a doctor immediately.

### **Caution**

1. If batteries do not perform or function well with certain equipment, refer to the instruction manual or warnings of the equipment.
2. Do not strike or drop batteries. Sharp impacts or concussions to batteries may result in leakage, heat generation and bursting.
3. Do not mix charged and discharged batteries together as this may cause leakage or heat generation.
4. Do not use old batteries with new ones as this may cause leakage or heat generation.
5. Do not use batteries with any other battery type, including dry cell, or with those of different capacity or brand. Mixed-matching of batteries may result in leakage, heat generation and bursting.
6. When more than two batteries are to be used together, charge them simultaneously prior to use.
7. Do not connect batteries in parallel as this may cause leakage, heat generation and bursting.
8. Children should not use batteries unless they have been carefully instructed and their parents or guardians have confirmed that the children understand and appreciate the proper usage and safety hazards presented by the batteries.
9. Store batteries out of the reach of small children. Ensure that small children cannot remove the batteries from the charger or equipment. There is no substitute for proper adult supervision.
10. Always follow the specified charging temperature ranges. Failure to observe the temperatures indicated, may cause leakage, heat generation and a decrease in performance or operating life of batteries.
11. For the recommended charging method for batteries, read the battery charger's instruction manual carefully.
12. Do not charge batteries beyond the recommended time described in the instruction manual for charger or equipment. Overcharging causes leakage and heat generation.
13. Do not carry the batteries by the connector or their lead wires as this may damage the batteries.
14. Be sure to turn off the equipment after use of batteries, as this may result in leakage.
15. After they have been removed from equipment, store batteries in a dry place and within the recommended storage temperature range. This will help preserve the batteries' performance and durability and to minimize the possibility of leakage or corrosion. (A temperature range from 10°C (50°F) to 30°C (86°F) is recommended for longer product life).
16. If the battery terminals become dirty, clean them with a soft dry cloth prior to use. Dirt on the terminals can result in poor contact with the equipment, loss of power, or inability to charge.

17. If corrosion, heat generation or other abnormalities are detected when using new batteries, immediately stop using them and return them to the store that they were purchased from.

## APPENDIX F

### Examples of Battery Chargers, State of Charge Indicators and Battery Protection Circuits

#### *Battery Chargers*

<a href="#"><u>BQ2000</u></a>	Multi-Chemistry Switchmode Charge Management IC with Peak Voltage Detection Termination
<a href="#"><u>BQ2000T</u></a>	Multi-Chemistry Switchmode Charge Management IC with dT/dt Termination
<a href="#"><u>BQ2002</u></a>	NiCd/NiMH Gating Charge Management IC with Negative dV and Peak Voltage Detection Termination
<a href="#"><u>BQ2002D</u></a>	NiCd/NiMH Gating Charge Management IC with dT/dt Termination
<a href="#"><u>BQ2002T</u></a>	NiCd/NiMH Gating Charge Management IC with dT/dt Termination
<a href="#"><u>BQ2003</u></a>	NiCd/NiMH Switchmode Charge Management IC W/Negative dV, dT/dt Termination
<a href="#"><u>BQ2004</u></a>	NiCd/NiMH Switchmode Charge Management IC W/Negative dV, Peak Voltage Detection, dT/dt Termination
<a href="#"><u>BQ2005</u></a>	NiCd/NiMH Switchmode Charge Management IC for Sequential Charging of Dual Battery Packs
<a href="#"><u>BQ2031</u></a>	Lead-Acid Switchmode Charge Management IC with User-Selectable Charge Algorithms
<a href="#"><u>BQ2054</u></a>	Li-Ion Switchmode Charge Management IC
<a href="#"><u>BQ2057</u></a>	Li-Ion Low-Dropout Linear (4.1V) Charge Management IC for One-Cell Applications with AutoCompTM
<a href="#"><u>BQ24001</u></a>	Li-Ion Linear (4.1V & 4.2V) Charge Management IC for One-Cell Applications W/Integrated FET, One LED
<a href="#"><u>BQ24003</u></a>	Li-Ion Linear (4.1V & 4.2V) Charge Management IC for One-Cell Apps W/Integrated FET, Bi-Color LED
<a href="#"><u>BQ24004</u></a>	Li-Ion Linear (8.2V & 8.4V) Charge Management IC for Two-Cell Apps W/Integrated FET, One LED
<a href="#"><u>BQ24007</u></a>	Single-Cell Li-Ion Charger for PDAs/Internet Appliances, Integrated FET, LED
<a href="#"><u>BQ24010</u></a>	bqTINY(TM) Linear, 1-cell (4.2V) Li-Ion Charger w/ 1-A FET, AC Present and Temp. Sense in QFN/MLP-10
<a href="#"><u>BQ24013</u></a>	bqTINY(TM) Linear, 1-cell (4.2V) Li-Ion Charger w/ 1-A FET, Charge & Term Enable in QFN/MLP-10
<a href="#"><u>BQ24023</u></a>	bqTINY-II 1-Cell Li-Ion Charger w/USB/AC Supply Mgmt in 3x3mm2 QFN-10 w/Enable, Timer/Term Enable
<a href="#"><u>BQ2402X</u></a>	bqTINY-II Single-Chip 1-Cell Li-Ion Charger w/USB/AC Supply Mgmt Family
<a href="#"><u>BQ24201</u></a>	500-mA, 4.1-V Single-Chip Li-Ion Charger for Current-Limited App. w/ Temp. Sense, MSOP-8
<a href="#"><u>BQ24204</u></a>	500-mA, 4.2-V Single-Chip Li-Ion Charger for Current-Limited App., MSOP-8
<a href="#"><u>BQ24205</u></a>	500-mA, 4.1-V Single-Chip Li-Ion Charger for Current-Limited App., MSOP-8
<a href="#"><u>BQ24400</u></a>	Programmable NiCd/NiMH Fast-Charge Management Device
<a href="#"><u>BQ24702</u></a>	Multi-Chemistry Battery Charge Controller and System Power Selector
<a href="#"><u>BQ24901</u></a>	Single-cell Li-Ion/Li-Pol Charger for Offline Applications (Primary-side Control) in TSSOP-14
<a href="#"><u>BQ2954</u></a>	Li-Ion Switchmode Charge Management IC
<a href="#"><u>DS2770</u></a>	Battery Monitor and Charge Controller
<a href="#"><u>ISL6291</u></a>	Battery Charger, Li-ion, Li-Polymer, 4.1/4.2V, Programmable Current Limit, 1% Accuracy
<a href="#"><u>ISL6292</u></a>	Battery Charger, Single Cell Li-ion or Li-Polymer, Vin >2.4v, Programmable Current Limit, Low Thermal Dissipation, 1% Accuracy

**Battery Chargers (continued)**

<a href="#"><u>LM3420</u></a>	Lithium-Ion Battery Charge Controller
<a href="#"><u>LM3621</u></a>	Single Cell Lithium-Ion Battery Charger Controller
<a href="#"><u>LM3647</u></a>	Universal Battery Charger for Li-Ion, Ni-MH and Ni-Cd Batteries
<a href="#"><u>LP3945</u></a>	Battery Charge Management System
<a href="#"><u>MAX1501</u></a>	Highly Integrated, Linear Battery Charger with Thermal Regulation for Portable Applications
<a href="#"><u>1507</u></a>	Linear Li <sup>+</sup> Battery Charger with Integrated Pass FET and Thermal Regulation in a 3mm x 3mm Thin DFN
<a href="#"><u>MAX1535</u></a>	Highly Integrated Level 2 SMBus Battery Charger
<a href="#"><u>MAX1645A</u></a>	Advanced-Chemistry-Independent, Level-2 Battery Chargers with Input Current Limiting
<a href="#"><u>MAX1647</u></a>	Chemistry-Independent Battery Chargers
<a href="#"><u>MAX1736</u></a>	SOT23, Single-Cell Li <sup>+</sup> Battery Charger for Current-Limited Supply
<a href="#"><u>MAX1737</u></a>	Stand-Alone Switch-Mode Lithium-Ion Battery-Charger Controller
<a href="#"><u>MAX1757</u></a>	Stand-Alone, Switch-Mode Li <sup>+</sup> Battery Charger with Internal 14V Switch
<a href="#"><u>MAX1772</u></a>	Low-Cost, Multichemistry Battery-Charger Building Block
<a href="#"><u>MAX712</u></a>	NiCd/NiMH Battery Fast-Charge Controllers
<a href="#"><u>MAX745</u></a>	Switch-Mode Lithium-Ion Battery-Charger
<a href="#"><u>MAX846A</u></a>	Cost-Saving, Multichemistry, Battery Charger System
<a href="#"><u>UC2906</u></a>	Lead-Acid Linear Charge Management IC
<a href="#"><u>UC2909</u></a>	Lead-Acid Switchmode Charge Management IC With Differential Current Sense
<a href="#"><u>UCC3956</u></a>	Li-Ion Switchmode Charge Management IC With Differential Current Sense

**Battery Gas Gauges**

<a href="#"><u>BQ2010</u></a>	NiCd/NiMH Gas Gauge with 1-Wire (DQ) Interface And 5 LED Drivers
<a href="#"><u>BQ2011</u></a>	NiCd Gas Gauge for High Discharge Rates (>5A), Small Pack Capacities (<2Ah)
<a href="#"><u>BQ2012</u></a>	NiCd/NiMH Gas Gauge with 1-Wire (DQ) Interface, 5 LED Drivers And Slow-Charge Control
<a href="#"><u>BQ2013H</u></a>	NiCd/NiMH/Lead-Acid Gas Gauge for High Discharge Rates (>10A), Pgmable Offset Error & Load Comp.
<a href="#"><u>BQ2014</u></a>	NiCd/NiMH Gas Gauge W/1-Wire (DQ) I/F, 5 LED Drivers, Control Signals for BQ2004 Fast-Charge IC
<a href="#"><u>BQ2016</u></a>	NiCd/NiMH Gas Gauge for High Discharge Rates (>5A), with Pack Capacities (<5Ah)
<a href="#"><u>BQ2040</u></a>	Multi-Chemistry Smart Battery System (SBS) 1.0 Compliant Gas Gauge with 4 LED Drivers
<a href="#"><u>BQ2050</u></a>	Li-Ion Gas Gauge with 1-Wire (DQ) Interface and 5 LED Drivers
<a href="#"><u>BQ2050H</u></a>	Li-Ion Gas Gauge with High-Speed 1-Wire (HDQ) Interface and 5 LED Drivers
<a href="#"><u>BQ2052</u></a>	Primary Lithium Gas Gauge W/High-Speed 1-Wire (HDQ) Interface, 3 Prgmable LED Patterns
<a href="#"><u>BQ2060</u></a>	Multi-Chemistry SBS 1.1 Compliant Gas Gauge with 5 LED Drivers, Additional Battery Mgmt Control
<a href="#"><u>BQ2063</u></a>	Li-Ion SBS 1.1 Compliant Gas Gauge with Protector Interface
<a href="#"><u>BQ2083</u></a>	SBS Compliant Gas Gauge IC for Use with BQ29311
<a href="#"><u>BQ2085</u></a>	SBS 1.1 Compliant Gas Gauge with Integrated Oscillator for Use with the bq29311
<a href="#"><u>BQ20851</u></a>	V1P2 SBS-Compliant Gas Gauge IC for Use with the bq29311
<a href="#"><u>BQ2092</u></a>	Multi-Chemistry SBS 0.95 Compliant Gas Gauge with 4 LED Drivers
<a href="#"><u>BQ26500</u></a>	Complete Battery Fuel Gauge for One and Two Cell Li-Ion Applications
<a href="#"><u>DS2751</u></a>	Multichemistry Battery Fuel Gauge

***Battery Protection***

<u>BQ29311</u>	3-, 4-Cell Lithium-Ion Protection IC for Use With BQ2083/5
<u>BQ29312</u>	Two, Three and Four Cell Lithium or Lithium-Polymer Battery Protection AFE
<u>BQ29400</u>	2nd Level Over Voltage Protection for 2, 3, or 4 Cell LiIon & LiPoly Batteries (2nd Lev Protection)
<u>DS2720</u>	Efficient, Addressable Single-Cell Rechargeable Lithium Protection IC
<u>UCC3911-1</u>	2-Cell Lithium-Ion Battery Protection IC W/Internal FET and Vov = 4.20V
<u>UCC3911-3</u>	2-Cell Lithium-Ion Battery Protection IC W/Internal FET and Vov = 4.30V
<u>UCC3952-1</u>	Single Cell Lithium-Ion Battery Protection IC W/Internal FET and Vov = 4.20V
<u>UCC3952-2</u>	Single Cell Lithium-Ion Battery Protection IC W/Internal FET and Vov = 4.25V
<u>UCC3952-4</u>	Single Cell Lithium-Ion Battery Protection IC W/Internal FET and Vov = 4.35V
<u>UCC3957-1</u>	3-, 4-Cell Lithium-Ion Protection IC W/Vov = 4.20V
<u>UCC3957-3</u>	3-, 4-Cell Lithium-Ion Protection IC W/Vov = 4.30V

## APPENDIX G

### 1. Battery Companies\*

**A&T Battery Company (Japan).** Asahi Chemical and Toshiba joint venture to produce Li-ion cells. In 2000, Toshiba acquired Asahi's interest.

**ATL (Amperex Technology Ltd, Hong Kong).** Produces Li-ion polymer batteries.

**Battery Technologies (Canada).** Develops and licenses rechargeable alkaline Zn/MnO<sub>2</sub> battery technology to Rayovac and others worldwide.

**BYD Battery (China).** Produces all types of batteries. Now rated the 3<sup>rd</sup> world producer.

**Duracell (USA).** Manufacturer of small primary batteries for the commercial market using alkaline manganese, lithium, silver oxide and air cell systems. Resells rechargeable batteries made by other producers. Division of Gillette.

**E-One Energy (Taiwan).** In the year 2000, acquired NEC-Moli Energy, the first manufacturer of rechargeable Li batteries (Li-MoS<sub>2</sub> system). Started production of Li-ion cells in 1994.

**Energizer Battery Company (USA).** Formerly Eveready. Major manufacturer of primary batteries: Zn-C, standard alkaline, silver oxide, lithium and air cell systems.

**Fuji Electrochemical (Japan).** Early producer of Zn-C and alkaline batteries. Now also producing Li-ion cells. Present name: FDK.

**GP Batteries (Hong Kong).** Produces primary and Ni-MH cells under the Gold Peak name. Will also make Li-ion cells using Duracell's technology and facilities.

**Hitachi-Maxell (Japan).** Produces Zn-C, alkaline and a variety of coin and button cells. A major producer of small thionyl chloride cells for memory backup. Produces Li-ion cells.

**Japan Storage Battery (JSB, Japan).** Major producer of Pb-acid in Japan. Joint venture with SAFT for Ni-Cd and Ni-MH. Produces Li-ion cells with its subsidiary GS-Melcotec. In 2002, Sanyo has acquired 51% of GS.

**LG Chemical (Korea).** Produces Li-ion batteries.

**Lishen Battery (China).** Produces most battery types.

**Matsushita Industrial Battery Company (Japan).** A full line battery supplier, producing: Pb-acid, Ni-Cd, Zn-C, alkaline, Zn/air, Li/CF<sub>x</sub>, Li/MnO<sub>2</sub>, Ni-MH, Li-ion, Zn/silver oxide. Joint venture with Kodak in the USA and Philips in the Netherlands. Matsushita products provide an in house OEM market for batteries.

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\*Adapted from Ref. 15

Markets under the **Panasonic** name and aims to be the world's largest battery company.

**NEC (Japan).** Produces prismatic Li-ion cells including those with  $\text{LiMn}_2\text{O}_4$  cathodes.

**Ovonic Battery (USA).** Now Texaco-Ovonic. Division of Energy Conversion Devices. Produces Ni-MH batteries. Joint venture with Texaco in 2000 for Ni-MH batteries and for fuel cells (Texaco acquired by Chevron in 2002).

**Polaroid (USA).** Makes thin flat Zn-C cells for use in film packs.

**Promeon, Division of Medtronics (USA).** Manufacturer of  $\text{Li/I}_2$ ,  $\text{Li/SOCl}_2$ ,  $\text{Li/SVO}$  and  $\text{Li/MnO}_2$  cells for implantable and other medical applications.

**Rayovac (USA).** Primary cells: Zn-C, alkaline, Zn/silver oxide,  $\text{Li/CF}_x$  and air systems. Introduced rechargeable alkaline cells in 1993.

**Renata (Switzerland).** Manufactures miniature cells for the watch industry.

**SAFT (France).** Specialized in industrial, OEM and military batteries, including all rechargeables. Acquired Tadiran (Israel) in 2000.

**Samsung (SMI, Korea).** Supplier of primary and advanced rechargeable batteries.

**Sanyo (Japan).** World's largest battery company. Early producer of Ni-Cd and Ni-MH cells, claims 40% of Ni-Cd and 70% of Ni-MH world markets. Also a major producer of Li-ion batteries.

**Seiko (Japan).** Produces coin and button cells in a number of systems, mainly for internal use in watches.

**Sony EnergyTec (Japan).** Produces small sizes of premium Zn-C and alkaline cells plus coin and button cells with Zn and Li anodes. Initial developer of the Li-ion batteries, which are used in all Sony's products. Claims to produce more than 40% of the world's Li-ion batteries.

**TCL Hyperpower Batteries (China).** Produces different types of batteries, including Li-ion.

**Toshiba (Japan).** A major producer of Zn-C and alkaline cells plus Ni-MH, Ni-Cd and Zn/Air. Acquired Asahi Chemical's share of A&T (see above) for Li-ion cells in 2000.

**Ultralife Batteries (USA).** Acquired Eastman Kodak's  $\text{Li/MnO}_2$  technology for primary batteries. Manufactures primary Li batteries and Li-ion batteries.

**Valence Technology (USA).** Manufacturer of Li-ion polymer batteries.

**Varta Microbatteries (Germany).** Manufacturer of miniature batteries (several systems) for mobile communication, medical and electronic equipment.

**Wilson Greatbatch (USA).** Manufacturer of Li batteries for medical and special commercial applications. First producer of batteries for implantable defibrillators.

**Yuasa Battery (Japan).** Producer of Pb-acid (also VRLA), Ni-Cd and Ni-MH.

## **2. Fuel Cell Companies**

**Ball Aerospace Technologies (USA)**  
**Ballard Power (Canada)**  
**Casio (Japan)**  
**Chevron-Texaco (USA)**  
**DCH Technologies (USA)**  
**Fuel Cell Energy (USA)**  
**Fuji Electric (Japan)**  
**Hydrogenics (Canada)**  
**Johnson Matthey (USA)**  
**Manhattan Scientific (USA)**  
**Matsushita Electric (USA)**  
**Medis Technologies (USA)**  
**Millennium Cell (USA)**  
**Motorola (USA)**  
**MTI MicroFuel Cells (USA)**  
**Neah Power Systems (USA)**  
**NEC/Fujitsu (Japan)**  
**Nuvera (USA)**  
**Plug Power (USA)**  
**Sanyo Electric (Japan)**  
**Siemens-Westinghouse Fuel Cell Systems (USA)**  
**Smart Fuel Cell AG (Germany)**  
**Toshiba International**

## **3. Supercapacitor Companies**

**Batscap (France)**  
**Cap-XX PTY (Australia)**  
**Cooper/PowerStor (USA)**  
**Danionics (Denmark)**  
**Econd (Russia/USA)**  
**ECR (Israel)**  
**Elit (Russia)**  
**Elna (Japan/USA)**  
**Epcos (Germany/Japan)**  
**Esma (Russia)**  
**Evans Corp. (USA)**  
**Hohsen (Japan)**  
**IMRA (USA)**



**Kanebo (Japan)**  
**Kyocera (AVX) (Japan)**  
**Matsushita (Panasonic) (Japan)**  
**Maxwell Technologies (USA)**  
**Montena (Switzerland)**  
**Motorola (USA)**  
**NEC/Tokin (Japan/USA)**  
**Ness (Korea)**  
**PRI (USA)**  
**SAFT (France)**  
**Samyoung (Korea)**  
**Superfarad (Sweden/Ukraine)**

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# Subject Index

- Acronyms used in electronics 262
- A/D converter 177
- AC/DC converter 169
- Anode, definition 1
- Alkaline primary batteries 39-47
  - advantages over Zn-carbon 39
  - applications 47
  - cell construction 42-3
  - commercial button cells 44
  - commercial standard cells 44
  - comparison with Zn-carbon batteries 46-8
  - tests of AA cells 48
- Alkaline rechargeable batteries 109-14
  - commercial types 110
  - cycle life vs. DOD 111
  - self-discharge 113
  - sizes 113
- Batteries (see also specific batteries)
  - alkaline primary 39-47
  - cardiac rhythm management 147-53
  - characteristics and applications 23-6
  - charging 167-86, 280-1
  - chemistry vs. management 180-3
  - collection/recycling 225-46
  - comparison with fuel cells 209
  - criteria of choice 22
  - designation 29-31
  - gas gauges, commercial circuits 281
  - glossary 263-9
  - handling 163-4
  - implantable 147-56
  - life cycle analysis 225-30
  - lithium primary 55-75
  - management 167-184
  - manufacturers 283-4
  - market 247-58
  - medical applications 147-56
  - microsensors 156-9
  - performance factors 10, 22
  - performance tests 31-2
  - primary aqueous, comparison 55-6
  - primary, designation 29-31
  - protection, commercial circuits 282
  - safety 163-6, 270-9
    - categories 187-8, 191
    - international agencies 187
    - tests and certifications 186-91
  - secondary 77-146
    - characteristics 79
    - comparison 144, 146
    - ranking 81
  - smart cards and tags 160-1
  - smart with SMBus 177
  - solid state 156
  - special applications 156-62
  - standard and sizes 29-31
  - standard electrode potentials 259-60
  - transportation rules 188-9
- Cathode, definition 1
- Cell
  - bobbin type 12
  - button 12, 14
  - design 12, 13
  - laminate (pouch) 13
  - prismatic 12
  - spirally wound 12
- Cells
  - connections 14
  - practical 7
- Cells and batteries, components 1
- Certification agencies 187
- Charge rate 7
- Charge/discharge efficiency 8
- Chargers 167-9, 184-6
  - commercial 184-6, 280-1
  - linear regulator 167
  - multichemistry 168, 180-1
  - smart-battery compliant 173-5
  - switching regulators 168-9
- DC/DC converter 169-70
- Depth of discharge (DOD) 8
- Discharge rate 8
- Electrochemical equivalent 2, 6
- Electrode,
  - polarization 7
  - selection criteria 2



- Electronic battery control 166-84
- Energy vs. current for primary and secondary batteries 21
- Energy density 20
- Faraday 6
- Fuel cells 193-210
  - cell stack 198-200
  - comparison with batteries 209
  - cost 202, 210
  - direct methanol fuel cells (DMFC) 194, 195, 201-2, 205-8
  - hydrogen cells 196-200
  - manufacturers 285
  - miniaturization 205-6
  - proton exchange membrane fuel cells (PEMFC) 194-8
    - components 195-6
    - scheme 196
    - theoretical energies 194
  - prototypes 206-8
  - technical challenges 203-4
  - thermal management 204
  - water balance 204
- Fuzzy logic 179
- Glossary of definitions related to batteries 263-9
- Implantable medical devices 147-56
- Integrated circuits for battery management 167-70, 173-6
- International Electrochemical Commission (IEC) 29
- Lead-acid batteries 78-83
  - applications 82
  - charge 84
  - commercial types 84
  - effect of DOD on cycling 80
  - self-discharge characteristics 82-3
- Li/CF<sub>x</sub> batteries 63-6
  - commercial types 67
- Li/FeS<sub>2</sub> batteries 66-70
  - applications 69
  - section of cylindrical 69
- Li/I<sub>2</sub> battery in pacemakers 149-50
- Li/Li<sub>x</sub>MnO<sub>2</sub> secondary batteries 115-7
- Li/MnO<sub>2</sub> batteries 58-63
  - applications 65
  - commercial types 64
  - cross-sections of cells 61
  - storage 62
  - temperature effects 62
- Li/Nb<sub>2</sub>O<sub>5</sub> secondary batteries 117-8
- Li/S secondary batteries 118-9
- Li/SO<sub>2</sub> batteries 70-2
- Li/SOCl<sub>2</sub> batteries 72-4
  - bobbin-type characteristics 73-4
- Li/SVO batteries 150-2
- Li/V<sub>2</sub>O<sub>5</sub> secondary batteries 117
- Lithium batteries
  - medical applications 147-56
  - primary, classification 58
  - primary, comparison 75
  - secondary (Li-based anode) 114-9
- Lithium-ion batteries 119-44
  - applications 142-3
  - carbon electrodes 120-5
  - care of 143-4
  - cell construction and performance (liquid electrolytes) 129-36
  - charge/discharge efficiency 124
  - commercial types 136
  - comparison with Ni-Cd and Ni-MH 144, 146
  - general characteristics 119-20
  - graphite as negative electrode 121-4
  - liquid electrolytes 128-9
  - positive electrodes 125-7
  - safety tests 189-90
  - with polymer electrolytes 137-42
    - capacity retention vs. temperature 140
  - commercial types 143
  - cycle characteristics 141
  - laminated cells 139
  - types of conducting polymers 137-9
- Market trends 247-58
  - by application 250-2
  - general remarks 247-8
- Li-ion batteries 250-8
  - long-term demand forecast 256-7
  - major manufacturers 253
  - price 253-7
  - by nation 254
- nickel-cadmium batteries 249-52
- nickel-metal hydride batteries 249-52
- rechargeable batteries 248-58
- Mechanical and thermal safety devices 164-6

- Negative electrode, definition 1
- Nickel-cadmium batteries 83-96
  - applications 94
  - Cd migration effect 93
  - charge 90-1, 181-2
  - commercial types 95
  - comparison with Ni-MH batteries 97-8
  - cycle life 93-4
  - electrode reactions, scheme 85
  - fibrous electrode 87
  - foam Ni substrate 87
  - gas recombining mechanism 86
  - recycling 237-9
  - self-discharge 89-90
  - sintered Ni substrate 86-7
  - temperature effect on capacity 89
  - temperature effect on charge, discharge, storage 91-2
- Nickel-metal hydride batteries 96-109
  - AB<sub>3</sub> alloy, improvements 100
  - alloys negative electrode 98-100
  - charge 104-7, 181-2
  - commercial cylindrical cells 110
  - comparison with Ni-Cd batteries 97-8
  - construction of a thin prismatic cell 102
  - cycle and battery life 107-8
  - discharge curves at various rates 102
  - electrode reactions, scheme 99
  - recycling 237-9
  - safety tests 188
  - temperature effect on charge, discharge and storage 103-9
- Open circuit voltage 3
- Polymeric positive temperature coefficient (PPTC) 183-4
- Portable devices 17-9
  - battery types 18, 23-26
  - current ranges 18
  - memory backup 19
- Positive electrode, definition 1
- Power management 169-84
- Recycling and collection 225-46
  - batteries from electronic waste 242-3
  - batteries in municipal waste streams (MWS) 231-3
  - battery components and hazards 228
  - battery hoarding 232-3
  - battery sorting 233-6
  - campaigns to improve collections 233
  - LCA (life cycle analysis) 225-30
  - lead-acid batteries 241-2
  - lithium and lithium-ion batteries 238-41
  - nickel-cadmium and nickel-metal hydride batteries 237-9
  - primary aqueous batteries 236-7
  - regulatory issues in the U.S.A. and E.U. 243-6
  - toxicity of elements 226-7
- Safety 270-9
  - commercial circuits 282
  - general considerations 270
  - Li-ion 274-6
  - Li primary 273-4
  - Ni-Cd and Ni-MH 276-9
  - Pb-acid 271-2
  - Zn-carbon and alkaline 270-1
- SBS Implementers Forum 170
- Self-discharge (shelf-life) vs. temperature 21, 27
- Smart Battery System (SBS) 170-180
- Specific energy 7, 20
- Specific capacity 6
- Standard electrode potential 3, 259
- State of charge (SOC) 8, 178
- State of health (SOH) 166, 178
- Supercapacitors 210-223
  - advantages and limitations 218-9
  - applications 219-23
  - capacitance, energy, power 213-4
  - characteristics of commercial 215-7
  - comparison with batteries and conventional capacitors 211, 218
  - double-layer 212-4
    - carbon electrodes 216
    - scheme 212
  - hybrid 214-5, 217-8
  - manufacturers 285-6
  - nanomaterials 216-218
  - redox 214
  - time constant 214
- Symbols 261
- System Management Bus (SMBus) 170-7
  - levels 173
  - single wire or two-wire 171-2
- Zinc-carbon batteries 34-9
  - cell construction 35

- commercial cells 40
- comparison with alkaline batteries 46-8
- Leclanché, advantages 38
- zinc chloride, advantages 38
- Zinc-air batteries 52-5
  - applications 55
  - characteristics of button cells 55
  - cross-section 53
  - electrode reactions 53
- Zinc-silver oxide batteries 47-52
  - applications 49
  - commercial button cells 50